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Semiconducting Intermetallic Compounds

By L. PINCHERLE

Bedford College, University of London

and J. M. RADCLIFFE

Radar Research Establishment, Malvern

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§ 1. INTRODUCTION

THE aim of this article is to provide a compact report on the published data relating to the preparation, properties, theory and applications of the so-called semiconducting intermetallic compounds. These compounds have attracted attention in recent years mainly because of the possibility that they may prove more efficient in particular applications than germanium or silicon, and perhaps lead to quite new devices, particularly those with a high carrier mobility. Their physics is of more general interest however, both intrinsically and comparatively, in that they form a new group of compounds which can be set alongside better known examples of crystals, e.g. the metals and the alkali halides.

It has been known for a long time that a pair of metals may combine to form an intermetallic compound. In particular it was noticed that the electrical conductivity of sequences of alloys of these metals showed a sharp drop at compositions which satisfied simple chemical valence rules, and that the structure at these compositions was not metallic. There are other intermetallic compounds which have complicated formulae which show no obvious relation to the valencies of the component elements. These compounds always have metallic properties and will not concern us here. The boundary between the two types of intermetallic compounds is sometimes referred to as the 'Zintl boundary'. This is a line through the periodic system such that compounds of two elements one to the left and one to the right of the boundary are non metallic, whereas compounds of elements both on the left are metallic. The Zintl boundary is between Group III and Group IV but is not well defined in some parts of the periodic Table. The composition of crystals containing two metals can often vary within certain limits. The phase diagram shows that crystals with compositions which depart slightly from stoichiometry have a lower melting point, and may be considered as solid solutions of one of the metals in the pure compound. The curvature of the liquidus-solidus curve near the maximum is a measure of these solubilities.

The intermetallic compounds which are semiconducting owe this property to the fact that the number of states and the number of available electrons are such that the valence band comprises all the bonding states in Hund's sense, whereas the conduction band is formed by the anti-bonding states. This fact has the additional consequence that their chemical stability must be high, higher than in a metal phase in which some of the anti-bonding states would be occupied. Welker (1954) remarks that this stability is further increased by resonance between the covalent and ionic contributions to the bond which causes an increase of the gap width.

More recently, a specific 'semiconducting bond' has been postulated (Mooser and Pearson 1956 b), resulting from the presence of essentially covalent bonds. If a diatomic compound is to be a semiconductor, at least one atom of the two must acquire completely filled s- and p-shells, and in this respect it is quite different from a metallic compound. The other atom need not acquire completely filled shells, and the presence of

empty 'metallic' orbitals on one atom leads to metallic behaviour only if these atoms are bonded one to another. The covalent nature of the bond is indicated by the small difference in electronegativity between the two atoms of a semiconducting compound. This difference is, for instance, 0.5 in InSb, 0.6 in Mg_2Sn , 0.6 in Mg_3Sb_2 , 0.8 in Li_3Bi , 0.3 in CdSb.

This valence bond picture, unlike the energy band model, uses atomic properties only. It can also lead to new results. First we note that, through electron sharing, an atom cannot gain a number of electrons greater than its valency. Hence, complete octets can only occur in atoms of Groups IV to VII; thus all semiconducting compounds must contain elements to the right of the Zintl boundary. Furthermore the model leads to the relation

$$n_e/n_a + b = 8$$

where n_e is the number of valence electron per molecule, n_a the number of elements of Groups IV to VII in the molecule, and b the number of bonds formed by these elements with similar ones. For typical semiconductors of the various types we have for instance :

<i>Compound</i>	n_e	n_a	b
InSb	8	1	0
Li_3Bi	8	1	0
Mg_2Sn	8	1	0
CdSb	7	1	1
Mg_3Sb_2	16	2	0

This rule allows prediction of semiconductivity in a given compound from knowledge of the stoichiometric formula, and of the valency of the elements; knowledge of the crystal structure is necessary only if $b \neq 0$.

Chemical binding in semiconducting solids is discussed in detail by Krebs and Schottky (1954).

Even when confining attention to the semiconducting intermetallic compounds (S.I.C.), there is no firm rule for deciding which compounds to include under the term of 'intermetallic'. In this review we shall exclude all compounds in which one of the elements is on the right of Group V in the periodic Table, although, for instance, many tellurides might well be called intermetallic compounds. Conversely, some of the compounds included, such as the phosphides, may not be strictly 'intermetallic'. Some of the properties of semiconducting compounds of Group VI elements have been discussed by R. A. Smith (1953). We shall also ignore compounds between elements of groups IV and V, such as SnAs . These compounds have been little studied so far. Only the briefest mention will be made of the I-V compounds, for, though some of them have found important applications, particularly in photocathodes, there has been little systematic study of their properties in the bulk. The article will thus be devoted to three groups of compounds, the II-IV, II-V and III-V. The II-IV compounds are all homologues of Mg_2Sn , the III-V homologues of InSb, and the II-V are homologues either of Zn_3Sb_2 , or ZnSb , or ZnSb_2 .

The semiconducting properties of ternary compounds such as MgAgSb (Frost and Raynor 1950) have not been studied to our knowledge.

Excellent reviews and discussions of the S.I.C. have been given by Welker (1954, 1956). A more elementary one has been published by Cunnell and Saker (1954).

In the following sections we shall discuss the various properties of these materials on which experiments have been made or might be made, and also the way in which the data are related to the basic parameters, like the width of the forbidden gap and the effective mass tensor. A general discussion of these basic parameters will follow, and the remaining sections will deal with the various groups of S.I.C., and singularly with the more important compounds. It is assumed that the reader has a knowledge of the properties and theory of semiconductors, such as may be gained, for instance, from a study of Shockley (1950). Experimental techniques will not be discussed. A useful collection of the standard formulae for the determination of the characteristic quantities of a semiconductor from electrical, optical and magnetic experiments has been published by Busch and Winkler (1956).

§ 2. THE NATURE OF THE EXPERIMENTAL DATA

2.1. *X-Ray Diffraction Patterns*

The interpretation of x-ray diffraction photographs is usually straightforward, except perhaps when mixed crystals are studied, since the crystal structures which occur are simple ones.

The early experimenters reported discrepancies for various materials between the density deduced from the lattice parameters and that measured directly. In general the x-ray densities were larger (vacancies), but sometimes smaller (interstitials). Smakula *et al.* (1955) have made some very precise measurements on Si, Ge and two alkali halides, which lead to apparently significant values for the density of defects. It would be useful if they were repeated on some intermetallic compounds. In crystals with a degree of ionic binding, defects play an important role since they behave in many respects as impurities.

2.2. *Doping*

Techniques to achieve a controlled impurity content in S.I.C. have a long way to go before attaining the perfection that they have reached in the case of germanium. There are well established results only for the III-V compounds, where the same rules hold as for the group IV elements. Impurities appear to enter the lattice substitutionally, Group II elements such as Mg or Zn behaving as acceptors, and Group VI elements such as Se or Te as donors. It will be useful to the understanding of the structure of these substances to study the effect of doping with elements of Group IV. This has been done only in the case of InAs, in which they substitute In and act as donors. An atom of, say, Pb should act as acceptor on a site normally occupied by an atom of Group V and as donor

in the other site. Welker (1953) argues that a large atom, such as Pb, would substitute the larger ion, and thus would lie preferably in the In sites in InSb, making it n-type, but in the Sb sites in AlSb, making it p-type.

Substitution of one of the components with another element from the same column does not appear to have any marked effect on the electrical properties.

Little is known of the properties of interstitial foreign atoms, as well as of those of vacant lattice sites and interstitial atoms of the component elements. It is known, however, that some compounds, when first produced or zone-refined, are always of the same type, p or n. It seems probable that this is due to a loss of the element with the higher vapour pressure at the temperature at which the compound is formed. The vacant lattice sites thereby formed would behave as donors or acceptors, or traps, and the study of radiation effects may prove useful in elucidating this point. The only published results of experiments of this type are on InSb and GaSb (Cleland and Crawford 1954, 1955). Under neutron irradiation, both transmutation and disorder effects were observed (In has a large cross section for the capture of slow neutrons). Sn was produced by the transmutation and behaved as a donor, confirming Welker's speculations, since p-crystals became n. The defects produced by fast neutrons acted as electron traps in n-type material, but it is not known whether they act as acceptors in p-type crystals.

2.3. Conductivity

The variation of conductivity with temperature was for a long time the main tool in investigating the properties of semiconductors. It is still very useful in conjunction with other data in particular for determining in the extrinsic range the activation energies of impurity centres and in the intrinsic range the main energy gap E_G . For the latter purpose one uses the formula

$$\sigma = \text{constant } T^{3/2} (\mu_e + \mu_h) \exp (-E_G/2kT),$$

μ_e and μ_h being the electron and hole mobilities. Assuming $E_G = E_0 + \alpha T$, one sees that, by plotting $\ln \sigma$ against $1/2kT$, one obtains a line of slope E_0 , the energy gap at absolute zero. This holds strictly for intrinsic samples in which the mobility varies as $T^{-3/2}$, and for which E_G is in fact a linear function of T .† Not all these conditions are satisfied in general, and then the interpretation of experimental results requires care. For the S.I.C. with high electron mobility an important point is that one may find an apparently intrinsic behaviour when in fact there are appreciably more holes than electrons. As a consequence, p-type specimens show an apparent energy gap larger than the real one (Austin and McClymont 1954). In the extreme case it will be twice as large. The lines plotting $\ln \sigma$

† In general, even if it is a linear function in the range of temperatures over which the experiment was done, it will not continue to vary linearly right down to absolute zero, since the expansion coefficient vanishes at 0°K.

versus $1/2kT$ are not in fact straight. On increasing the impurity content, p-curves become steeper and are displaced towards smaller value of $1/2kT$, while n-curves become flatter and are displaced in the opposite direction. All these effects may be explained by standard theory if b , the mobility ratio, is large (Folberth and Madelung 1953).

It has become increasingly evident that the best determinations of E_G are the optical ones (§2.9), but a judicious combination of electrical and optical experiments gives a clearer picture of the situation.

2.4. Hall Coefficient

Measurement of the Hall coefficient R is important because in principle it is the most direct and sensitive measure of the number of carriers in the system. However the interpretation of the data is often difficult. The use of the Hall data to deduce the energy gap is subject to the same limitation as that of the conductivity data, and there is the further complication that R may depend on the magnetic induction B at such low field strengths that extrapolation to $B=0$ is uncertain. The theory of the variation of R with B depends on knowledge of several parameters, so that comparison with experiment is difficult for finite B . This dependence of R on B is found to be particularly marked in p-specimens near the temperature at which the Hall voltage changes sign (Weiss 1953). The effect has been demonstrated in an elegant experiment by Busch *et al.* (1955) using the magnetic field produced by the current in the specimen itself. Such a self-field of about 1 gauss in InSb at 77°K induced a Hall voltage corresponding to a value of R much higher than that obtained with applied fields of 10^3 – 10^4 gauss. Theories of the change of R with the magnetic induction have been given by Johnson and Whitesell (1953), Madelung (1953) and by Madelung and Welker (1953). It does not appear that these theories can account for all the effects that are observed.

In the region of mixed conduction the interpretation of Hall coefficient and resistivity data is laborious, and often unrewarding if the experimental results have been obtained on poor crystals, because the data then show such large scatter that it is not easy to decide how to correlate them. Various methods have been devised for the analysis of data (see e.g. R. A. Smith (1954)—others are based on fitting Dunlap's (1950) ellipse), but there is none of outstanding merit for all cases. The correction terms which come into play for degenerate samples have been given by Austin and McClymont (1954). A method especially suited to substances with a high mobility ratio has been given by Madelung and Welker (1953). At very high fields R saturates to the value $1/e(p-n)$ quite generally, whatever the band structure (Swanson 1955).

2.5. The Magnetoresistance

The fractional change of resistance in a magnetic field is equal, at low fields, to $\mu^2 B^2$, where, in impure specimens, μ is very nearly the mobility of the majority carriers and in intrinsic samples a combination of the

mobilities. Thus in principle this phenomenon permits a determination of mobilities, but its usefulness is limited by the fact that high fields are required unless the mobility is high, and by the inadequacy of the theory except in the simplest cases. The theory is expounded by Wilson (1953) and has been discussed more recently by McClure (1956) for a crystal with a general band structure, assuming that the Boltzmann equation is valid and that a relaxation time exists. This analysis has shown that the fractional change of conductivity is the same as would be shown by a superposition of electron gases whose cyclotron frequencies are related harmonically. The relative strength of the various harmonics depends on band structure. For a general discussion of the theory of galvanomagnetic effects in semiconductors see also Madelung (1955 a, b).

More important is the measurement of the anisotropy of the magnetoresistance, or rather of the magnetoconductance which can be compared more directly with the theory, because it provides information on the components of the effective mass tensor. However the published results on S.I.C. are scarce and sometimes conflicting.

The ordinary magnetoresistance effect is a function of the geometry of the specimen and may be increased by using a Corbino disc (Weiss and Welker 1954).

B. Lax and co-workers (unpublished) have suggested a very promising modification of the conventional arrangement. They propose to use a sensitive microwave bridge. With such a bridge it is possible to rotate the magnetic field with respect to the crystal axes. A study of the anisotropy using this bridge should give all the information which can be obtained with static experiments, but would avoid the problem of making contacts and of excluding thermal effects. It may also be of use on specimens which are too impure to show a resolved cyclotron resonance. The theoretical analysis (Herring 1955) is simplified because the conductance is measured directly. On the other hand it may be that the skin effect will be troublesome.

2.6. Resonance Experiments

The most direct way to determine the components of the mass tensor is to measure the cyclotron resonance frequencies as a function of the orientation of the crystal axes with respect to the magnetic field, i.e. to measure the frequencies resonating with the frequency with which the carriers circulate in their orbits perpendicular to the magnetic field. These frequencies are in the microwave region for applied magnetic fields of the order of 10^3 gauss. The quantum theory of this phenomenon has been discussed by Luttinger (1956). The resonance will be resolved only if the electron describes at least an appreciable fraction of an orbit between collisions, so that $\omega\tau \sim 1$. This means that very pure crystals must be held at temperatures in the helium range during the experiment. Since the density of thermally excited carriers is then extremely small, carriers must be created, usually by optical excitation.

This extremely elegant and promising method has however met a serious limitation when applied to S.I.C. The cyclotron resonance is obscured by a plasma resonance. The equation of motion of the electron is

$$m(i\omega' + 1/\tau)\mathbf{v} = e[\mathbf{E} + (1/c)\mathbf{v} \times \mathbf{B}],$$

where $\omega' = (\omega^2 - \omega_p^2)/\omega$ and ω_p is very near the classical plasma frequency $(4\pi e^2 n/m)^{1/2}$ and contains a depolarization factor which is a function of the shape of the specimen. The resonance occurs when the cyclotron frequency is equal to ω' . The difficulties which arise when trying to interpret the absorption spectrum, and possible ways in which they may be overcome are discussed by Dresselhaus *et al.* (1955 b). The only S.I.C. for which a resonance has been analysed is InSb (Dresselhaus *et al.* 1955 a). A plasma resonance was also observed in InSb, and nuclear magnetic resonances in InSb and GaSb.

It has often been suggested that the de Haas-van Alphen effect, another manifestation of the quantization of electron orbits in a magnetic field, might be used to study the Fermi surface and hence the effective mass tensor. No experimental results have been published. The interpretation of results would probably be very difficult.

An effective mass may in principle be determined from the ionization energy of impurity centres, if the dielectric constant is known, by assuming validity of the hydrogen atom formula. If the wave function of the ground state of the impurity does not differ much from that of the state at the edge of the band, this effective mass will be some average of the mass tensor at the edge.

Benedict and Shockley (1953) have determined a certain average of the mass tensor by observing the frequency at which the carriers can no longer respond to an alternating field because of their inertia. The combinations of the three principal effective masses which appear in the formula relating to this experiment and in the expressions for various other physical quantities such as the change of the Hall coefficient with B , have been discussed, under fairly general assumptions, by Herring (1955) (*q.v.* for earlier references). Theoretical and experimental problems concerning effective masses have been discussed by Seraphin (1955).

2.7. Piezoresistance

Instead of producing an anisotropy by application of a magnetic field, one can apply a strain to the crystal (C. S. Smith 1954). The resistance changes, mainly because of shifts, induced by strain, of the band edges, and from the directional dependence of this effect information may be gained on the mass tensor (Herring 1955). These experiments are difficult both to perform and to interpret.

2.8. Magnetic Susceptibility

A theoretical treatment of the various contributions (by the atoms, the free carriers and the impurities) to the magnetic susceptibility of a

semiconductor has been given by Busch and Mooser (1953). The diamagnetism due to the free carriers is temperature dependent, hence can be separated from the atomic contribution in pure specimens, and its temperature variation reflects that of the free carrier density. From its study one can thus get values for the activation energy. One can also, in some cases, have an indication of the effective masses. As shown by the same authors in the case of grey tin, the behaviour of the susceptibility of impure specimens is characteristic of the type of centres: one can thus study which centres arise from the introduction of given foreign atoms. Among S.I.C. this method has been applied only to InSb (Stevens and Crawford 1955). The susceptibility is generally small and measurements are difficult. The separation of the various contributions also may not be straightforward.

2.9. Optical Experiments

These are proving increasingly powerful in the study of the fundamental properties of semiconductors. Ultra-violet spectra are not important, and for most compounds the interest centres in the infra-red. High resolution monochromators and a variety of very sensitive detectors are now available for this region. Experiments are generally concerned with absorption and reflectivity, except in the study of the radiation emitted during recombination of injected carriers. It has been suggested that a study of the Faraday effect in the infra-red may give information on the effective mass of the free carriers (Mitchell 1955).

The absorption experiments give the position of the main absorption edge with a high accuracy, and hence the value of the energy gap. Difficulties in defining exactly the edge of the absorption have been removed by the theoretical analysis of Macfarlane and Roberts (1955). No S.I.C. shows absorption with formation of excitons, photoconductivity extending to the absorption limit. Absorption experiments also give information on impurity levels, not only on the ionization energy of the centre, but also on the transitions between its hydrogen-like energy levels; on intra-band transitions, when a band consists of several branches; on the main lattice absorption, generally in the far infra-red; and on the change with temperature of all these quantities. The methods used involve in principle the determination of both the transmission and the reflection coefficients of thin plates, but different techniques have been used by different experimenters, e.g. by Oswald and Schade (1954) and by Roberts and Quarrington (1955). Results must be corrected, among other things, for multiple reflections and for the finite width of the slit. These methods give also the value of the refractive index and its variation with wavelength. The behaviour of n follows qualitatively classical dispersion theory. In the case of powdered semiconductors the absorption edge may be determined from the diffuse reflection spectrum: this shows a marked increase in intensity when the particles become relatively transparent (Fochs 1956).

By combining the optically determined energy gap with the density of intrinsic carriers determined from Hall effect measurements it is possible to obtain a value for the product of electron and hole effective masses, $m_e^* m_h^*$. It is necessary to know the number of equivalent minima in the bands and also the rate at which E_g varies with T . These values usually are only an indication of the order of magnitude of the effective masses, useful as a check of other determinations.

Besides the absorption due to electron transitions between quantized levels or bands, there is an absorption due to the conducting carriers. According to classical theory, this absorption should be proportional to the square of the wavelength and inversely proportional to the effective mass which occurs in the mobility. However there is no complete discussion of this absorption in quantum theory†. It is indeed found that the free carrier absorption is high in substances with a small effective mass, but the λ^2 law has not been verified in S.I.C. In the most carefully investigated one, InSb, n- and p-type specimens showed quite different spectra, and neither obeyed the λ^2 law except at very long waves (Avery *et al.* 1954, Kaiser and Fan 1955). These phenomena are still unexplained.

The lattice absorption spectrum is of interest because it yields directly the energy of the optical modes of lattice vibration, and its magnitude depends on a fluctuating dipole moment which in turn is a function of the type of bonding in the crystal. As yet no theory of the lattice absorption spectrum of the S.I.C. has been developed.

Although obeying roughly the law of variation with $(E - E_g)$ appropriate to indirect (optically forbidden) transitions, the rate at which the absorption constant K varies with E near the main edge is very different in different compounds: for example the edge is very steep in GaSb while is flat in Mg_2Sn . If E_1 is the energy of the conduction band at the position in momentum space occupied by the holes, and E_0 is the energy of the bottom of the band, second order perturbation theory shows that dK/dE is very roughly inversely proportional to $(E_1 - E_0)^2$ (Hall *et al.* 1954). If this is indeed the relevant factor, the steepness of the edge would not be of very fundamental importance.

The radiation emitted in the recombination of added carriers (the inverse process to inter-band absorption) is generally weak because radiative transitions have to compete with transitions with emission of phonons, recombination through traps (Shockley and Read 1952, Haug 1954) and, in impure samples, with Auger transitions (Pincherle 1955 b). The total recombination rate, assuming the transition probability to be independent of energy, is given by Allen and Mackintosh (1955) as $(E - E_g)^2 \exp(-E/kT)$ for light of frequency E/h . No attempt has been made so far at interpreting theoretically the few experimental results.

† *Note added in proofs.*—The theory of the high frequency conductivity in semiconductors has now been given by Donovan and March (*Proc. Phys. Soc. B*, **69**, 528, 1956) for both lattice scattering and impurity scattering, using classical statistics and spherical energy surfaces.

These show that the peak of the line emitted (which may be fairly narrow and, particularly in InSb, may become a good source of almost monochromatic infra-red radiation) is at about $E=E_G$, while the spectrum extends appreciably towards longer waves, showing that the radiative transition may be accompanied by the emission of a number of phonons, or occur between the main bands and trapping centres. A review of radiative transitions in semi-conductors has been published by Reichardt (1955).

2.10. Rectifying Properties

All S.I.C. rectify in some degree. Some have very high rectification ratios and can stand high back voltages. Although p-n junctions have been grown in some compounds, there has been no systematic study of their characteristics, nor of the properties of metal point contacts. Injection of minority carriers is difficult to achieve, and a possible transistor effect has been reported only in InP and InSb.

2.11. Photoconductive, Photovoltaic and Photoelectromagnetic Effects. Lifetimes

The main purpose of these experiments is to determine the bulk lifetime and surface recombination velocity of added carriers, vital quantities for practically all applications. Photovoltaic effects arise at p-n junctions and other potential barriers created artificially or accidentally in the crystal, and at metal-semiconductor contacts. Approximate values of the energy gap and of impurity activation energies are also obtained from a study of these phenomena.

Photoconductivity theory, encompassing homogeneous as well as heterogeneous models, and covering the processes of electron and hole generation, recombination, drift, diffusion and trapping has been treated by Rittner (1955 ; see also various papers in the *Proceedings of the Atlantic City Conference on Photoconductivity*, to be published.) The photoelectromagnetic (P.E.M.) effect (arising when a S.C. subject to illumination I is placed in a magnetic induction B perpendicular to I : a voltage appears in the third perpendicular direction) has been treated theoretically by van Roosbroeck (1956), who deals also with the Dember, or photodiffusion effect, the voltage appearing in the direction of illumination, independently of the presence of a magnetic field, due to the different diffusion coefficients of electrons and holes.

Practically all research carried out on S.I.C. refers to InSb. Probably the simplest method of determining lifetimes is to measure both the photoconductive response and the P.E.M. effect in the spectral region in which they are practically independent of λ (Aigrain and Bulliard 1953). Their ratio is proportional to $(\tau/D)^{1/2}$, where D is the diffusion coefficient, ambipolar in intrinsic specimens, which may be calculated from the measured mobility by means of Einstein's relation $D=kT/e$ (if classical

statistics is applicable ; cf. Allen and Mackintosh 1955). By measuring also the absolute value of one of the two effects one can get also the surface recombination velocity s (Hilsum *et al.* 1955), defined by the equation $J=sp$, where J is the current density into the surface and p the density at the surface of the minority carriers. Note that if the number of added carriers is large and recombination on the surface follows the law of mass action, s is no longer a constant, but depends on p .

On approaching the long wave cut-off, the light will penetrate deeper into the specimen, and recombination at the front surface will lose importance. If it had been dominant in removing the added carriers, one may get a sharp increase of the photoconductive response near the edge, whereas the P.E.M. signal decreases steadily to the cut-off. These effects provide additional methods for measuring τ and s and the absorption coefficient K . A similar method, but using the photovoltaic effect instead of the photoelectromagnetic, has been suggested and worked out theoretically by Moss (1955). Yet another method may be provided by a study of the characteristics and of the photoconductivity of the 'magnetic rectifier' developed by Weisshaar and Welker (1953).

Light spot methods have been used by Avery and Jenkins (1955). Their theory has been treated by van Roosbroeck (1955). They suffer from the difficulties and objections well known for the case of Si and Ge. The decay of photoconductivity has always been found so short in S.I.C., that the only determination of lifetimes by this method is that of Kurnick *et al.* (1955) on InSb using a xenon spark source. An indication of the order of magnitude of the lifetime is given also by the intensity of the recombination radiation.

The lifetimes determined so far have been at the most of a fraction of a microsecond, but this is probably a property of the substance, InSb, on which the experiments have been carried out, because in InSb the radiative recombination lifetime is very short. It is likely to be larger in substances with a larger energy gap (§ 4.8). However it follows from the theoretical treatment of van Roosbroeck and Shockley (1954) that it cannot be very large when the absorption edge is very steep, as found in the III-V compounds.

Surface recombination velocities have been measured in InSb and found to be generally of the order of 10^6 cm/sec ; it has been possible however to reduce them to about 10^4 by suitable surface treatment.

Finally, from the dependence on B of the P.E.M. effect it is possible to deduce the mobility of minority carriers.

A review of photoeffects in intermetallic compounds has been published by Frederikse and Blunt (1955).

2.12. Thermoelectric Power (TEP)

The absolute TEP of a semiconductor is determined primarily by the position of the Fermi level, hence this position is essentially what is measured in TEP measurements. If the density of (intrinsic or extrinsic)

carriers has been found by means of other experiments, one can then obtain a value for the effective mass of the carriers in the extrinsic range, or for the ratio of electron to hole effective mass in the intrinsic region. When the mass is anisotropic, one obtains the overall value relative to conduction phenomena. The TEP is also used to determine whether conduction is of p- or n-type. A rough indication of the value of the energy gap may also be obtained, as the TEP reaches a maximum value ϕ which is connected to the energy gap by the approximate relation (Welker 1954) $\phi = E_g/eT$.

The theory, leading to a general expression for the TEP in terms of the Fermi level, energy gap, mobility ratio and effective masses has been given by Johnson and Lark-Horovitz (1953) (see also Lautz 1953). Simpler formulae for particular cases are given by these authors and are found in the literature. The theory for degenerate samples with lattice scattering only is discussed by Korenblit and Shraifel'd (1955 a, b). Values of effective masses in agreement with other determinations have been obtained by this method, e.g. in n-type InSb by Frederikse and Mielczarek (1955) on rather pure crystals, and by Mansfield (private communication) in degenerate samples with predominant impurity scattering. The method requires however very careful interpretation when more than one scattering mechanism is present, when the sample is near degeneracy and for complicated band structures. At low temperature the TEP should decrease linearly with T , but a new effect arises due to the drag that the phonons, diffusing much more freely at these temperatures, exert on the carriers. This effect, studied theoretically by Herring (1954), gives rise to very high values of the TEP at low values of T , and it makes it vary as $T^{-7/2}$, until limited by a saturation effect due to the finite dimensions of the specimen. From its study, information may in principle be obtained again on effective masses, and also on how crystal momentum distributes itself among the various modes of oscillation, but this information is likely to remain of a qualitative nature.

When both kind of carriers are present, another effect is envisaged by Price (1955), due to the difference in the diffusion coefficients of electrons and holes. The more mobile carriers diffuse more rapidly and an electric field is set up to equalize the velocities (the phenomenon is thus analogous to the Dember or photodiffusion effect (Moss *et al.* 1953)). The extra terms in the TEP due to this effect are quite large.

2.13. Thermal Properties

No specific heats of S.I.C. have been measured, and only a few thermal conductivities. The most interesting result is the very high thermal conductivity of InSb (§ 4.8). In semiconductors it is the electronic contribution to the thermal conductivity which is of interest, and its theory is well understood, whereas that of the lattice contribution is not (see, for example, Herring 1954). The theory of the contribution due to 'phonon drag' to the TEP requires a knowledge of the way in which the

mean free path of the phonons depends on temperature. The theory of this variation is very complicated, and in particular it depends critically on the symmetry of the lattice.

A phenomenon which has been little studied, but which could in principle yield interesting information, is the Nernst effect (the transverse voltage arising at right angles to a temperature gradient and a magnetic field). Price (1955, 1956), has given the theory and made suggestions on how to derive fundamental parameters from measurements of the effect (see also Putley 1955). The phonon drag causes an anomaly in the Nernst effect also.

§ 3. THE BASIC PARAMETERS

3.1. *The Energy Gap*

The energy gaps of the intermetallic compounds vary over a wide range. Despite several attempts, no well-founded and reliable way of determining the energy gap *a priori* has been discovered. The gap might be correlated with a number of parameters, perhaps most directly with the melting point. This is an empirical fact in the compounds under consideration, and may be explained by the fact that both quantities are influenced by the strength of the ionic bonding. Because of resonance between the homopolar and the ionic bond the binding is stronger and the melting point higher. At the same time E_G increases above the value corresponding to pure homopolar forces.

The infra-red refractive index does not appear to be sensitive to variations of E_G .

The most important rule states that in any given series, such as GaP, GaAs, GaSb, or AlSb, GaSb, InSb, the energy gap decreases with increasing atomic weight of the variable component. The only known exception to this rule in semiconductors is in the series PbS, PbSe, PbTe, where PbSe has the smallest gap. To justify this rule in a rough way, one may observe that, when the atoms are brought together to form a crystal, there is a lowering of the interatomic potential barriers so that, in a given series, the lower the barrier, the smaller will be the energy gap. As the interatomic equilibrium distances generally increase more slowly than the atomic radii, the barrier will be lower for heavier atoms, hence a smaller gap. Moreover, in a given series, the ionization energy of heavier atoms is smaller. Also the ionic component of the bond is smaller for heavier atoms and this will tend to reduce E_G . An additional consequence is a higher curvature of the energy surfaces, and hence smaller effective masses and higher mobilities.

In most S.I.C., and in particular in all the III-V compounds, the energy gap decreases with increasing temperature, as it does in Si and Ge, and contrary to what happens in PbS and related compounds. Of the compounds studied so far only Mg_2Sn appears to behave in this 'anomalous' way.

The variation of E_G with T is due to the combination of two effects, the change in lattice constant, and the temperature-dependent interaction with the lattice vibrations. The latter effect must always produce a decrease of the energy gap with increasing T . It is not a broadening of the levels in the bands, but a real shift. Theoretical treatments have been given by Fan (1951, see this paper for references to previous work) and, for polar crystals, by Fröhlich *et al.* (1950). The expansion effect has been investigated for homopolar substances by Shockley and Bardeen (1950) on the basis of their 'deformation potential'. The sign of the latter effect depends on whether the actual lattice distance is larger or smaller than that lattice distance at which the bands would cross. Both effects are thus related to the mobility, but no serious attempt has been made yet to see whether data on S.I.C. are fitted by any of the existing formulae.

3.2. The Band Structure

In general one can gain experimental information on the properties of the energy surfaces only within a range round kT of the band edge. Conversely, this is the only information which is needed for applications. An interesting exception is the conduction band of InSb which can be filled to an appreciable height by a relatively small density of electrons because of its extraordinarily high curvature (Burstein 1954, Moss 1954). The corresponding density of states has been studied experimentally by Barrie and Edmond (1955).

The band structure is thus sufficiently described by the effective mass tensor of each band edge and the position of that edge in the Brillouin zone. Information on these parameters is obtained most directly by a study of the cyclotron resonances as functions of the orientation of the magnetic field with respect to crystallographic directions, but, as already mentioned, it is doubtful whether it will be possible to apply this method to most S.I.C. Of much wider application appears the method suggested by Macfarlane and Roberts (1955), based on a study of the optical absorption edge at high resolutions in order to determine its shape as accurately as possible over a wide range of absorption constants. Pure crystals are necessary in order to eliminate the background absorption by free carriers or impurity centres. From the shape of the curve plotting K versus $(E - E_G)$, where $E = h\nu$, it is possible to decide whether the inter-band transition is optically allowed (Hall *et al.* 1954), since for optically allowed (direct) transitions K should behave near the limit as $(E - E_G)^{1/2}$ or $(E - E_G)^{3/2}$, whereas for forbidden (indirect) transitions (involving an interaction with the lattice) it should vary as $(E - E_G)^2$ or $(E - E_G)^3$. For indirect transitions it is also possible, at least for not too complicated band structures, to determine the energy of the lattice vibration which makes possible the otherwise forbidden transition by providing the balance of momentum. If the phonon spectrum is known, the distance in momentum space between the two main band edges may be estimated, and also the number of equivalent minima.

There is at present no way to obtain experimental data on the density of states through the main band, since the interpretation of soft x-ray experiments (Skinner 1939), which in principle could be expected to give such information, is not straightforward (Parratt and Jossem 1954); the method gives information mainly on certain types of impurity states, and only if and when these are understood in detail, on the main bands also.

In view of this, it is understandable that one tries to gain the required knowledge theoretically by means of the laborious band structure calculations. In these one strives by a variety of methods to obtain more or less from first principles the relation between energy and crystal momentum for the various bands allowed by the symmetry of the crystal. Confidence in this type of calculation has fluctuated in the last few years. While the advent of electronic computers has shown that all the various techniques (augmented plane waves, orthogonalized plane waves, cellular method, etc.) lead, after varying amount of labour, to the same band structure starting from a given potential, the strong dependence of the calculated structure on the potential itself is a disquieting feature. A proper consideration of exchange and correlations in determining the potential is still lacking: it would probably imply a not inconsiderable dependence of the potential on \mathbf{k} . This dependence could only be determined through a self-consistent calculation, but such refinements appear at the moment to be beyond the capacity of even the largest automatic computers.

3.3. *The Carrier Mobility*

This is given by the electrical experiments through the product $R\sigma$ (R =Hall coefficient, σ =conductivity), which has the dimensions of a mobility (Hall mobility) and in the extrinsic range is in fact not very different from the mobility found from the conductivity or from that which would be measured in drift experiments. However the ratio between Hall and drift mobilities depends on the scattering mechanism of the carriers and on the band shape. This ratio may also be a function of temperature. Unfortunately in all the S.I.C. investigated so far, injection of minority carriers is very inefficient, and their lifetime short, so that no drift mobilities have been measured. All the values quoted will thus be Hall mobilities. In the intrinsic range $R\sigma$ gives the difference $\mu_e - \mu_h$, while in the mixed conduction range the mobilities may be worked out by one of the methods mentioned in § 2.4. The ratio, which we denote by b , of electron to hole mobility is often determined from the zero or the minimum of the Hall coefficient of p-type specimens. This of course gives b at the corresponding temperature: there is evidence that b is generally a function of T (Howarth *et al.* 1956). This method suffers from the disadvantage that R varies with B even at low fields near the reversal point.

There has been much speculation on the factors which determine the carrier mobility in semiconductors, in particular on why the mobility of electrons should be so high in InSb (up to 80 000 cm²/voltsec at room temperature), and on why the mobility should increase with increasing atomic weight of the components. Writing the mobility formally as $\mu = e\tau/m^+$, where τ is a relaxation time and m^+ an effective mass, the high mobility may be due to high values of τ or to low values of m^+ . There is now no doubt that the effective masses are small, and this, as already remarked, could be expected on general grounds particularly for heavy atoms when the forbidden energy gap is small, because the relevant bands are of the same symmetry, cannot cross and repel each other producing a large curvature of the constant energy surfaces at the band edges. It is probably fortuitous that the hole mobility is smaller. It happens that at the point in momentum space corresponding to the top of the valence band the gap is bigger.

The effect on energy gap and curvature of the energy surfaces of an ionic component in the potential has been studied by Seraphin (1954) on a Krönig-Penney one-dimensional model with pairs of unequal potential wells supposed to represent the state of affairs along the (1,1,1)-direction in a crystal with the zincblende structure. On varying the ratio between the depths of the two wells from one (grey tin) to other values supposed to correspond to InSb, CdTe, AgI, he finds that, whereas the forbidden gap between the first and second band increases monotonically, the curvature of the E - k curve at the bottom of the second band reaches a minimum in correspondence of InSb. The very high mobility in InSb would thus be associated with a small ionic component of the bond reducing m^+ . However it is not certain that the low mass is the only cause of the high mobility. Goodman (1955) takes the opposite point of view that, at least for the III-V compounds, the high mobility is caused by a large τ (weak interaction with the lattice vibrations). In an interesting way of presenting the data, he tries to correlate the mobility with the ionic contribution to the energy gap E_{ion} , which is taken as a measure of the ionic contribution to the bond. E_{ion} is estimated by subtracting from the experimental energy gap a hypothetical covalent contribution deduced from the energy gaps of the Group IV elements (C, Si, Ge, Sn). E_{ion} plotted against lattice constant is assumed to increase monotonically with the Coulomb crystal energy, proportional to z^2/d , where z is the effective charge, and d the bond length. Thus the quantity $K = d^{3/2} E_{\text{ion}}^{1/2}$ should give a rough measure of the bond dipole. By plotting the experimental mobilities of the various compounds against K , all the points lie fairly well on one curve with a sharp maximum near InSb. It is suggested that this behaviour may be expected by observing that the addition of an ionic component of bonding will strengthen the bond, hence reduce the amplitude of the lattice vibrations, and the amount of lattice scattering by phonons. When the bond becomes more and more ionic in character, optical modes of oscillation become important

and the mobility is again reduced. Similar suggestions have been made by Welker (1952, 1953) and by Bruns and Lautz (1954).

Goodman himself points out possible objections to his views. Thus, besides ignoring any dependence of mobility on effective mass, the mobilities used refer only to room temperature and no account is taken of impurity scattering. Further, in correlating the energy gap with the lattice constant, the variation with temperature is ignored and, more seriously, the fact that the forbidden energy region is not limited by the same bands in the elements considered. Thus in Si the bottom of the conduction band is along the (1,0,0)-direction, while in Ge it is along (1,1,1).

Finally, adopting the model based on deformation potentials (Shockley and Bardeen 1950), the mobility is inversely proportional to the square of a factor measuring the shift in energy of the band edge per unit dilatation of the crystal. If it happened that in a crystal the position of one of the band edges were almost independent of lattice constant, the mobility of the corresponding carriers, in so far as determined by scattering by phonons, would be very large. No theoretical treatment has been given yet along these lines.

Further information on the scattering mechanism is provided by the temperature variation of mobility. As is well known, scattering by the acoustic modes of lattice vibration leads, with bands of normal form, to a $T^{-3/2}$ law, scattering by the optical modes to a law of the type $\exp(-\theta/T)$ below the Debye temperature θ , and scattering by impurities to an increase of mobility with increasing temperature. Now the exponential behaviour produced by scattering by the optical modes has never been observed in S.I.C. It looks as if there are always too many phonons for the optical modes to play any major role at any temperature. Above the Debye temperature the scattering by optical modes increases less rapidly with T than that due to the acoustical modes. This failure to observe any optical scattering speaks against the explanation of the high mobilities in terms of an optimum in the ratio of scattering by acoustical modes to scattering by optical modes.

The temperature variation found experimentally at high temperatures follows more or less the $T^{-3/2}$ law, though exponents larger than $3/2$ have been reported, e.g. in Mg_2Sn . Many justifications have been given for the occurrence of these high exponents, such as inter-valley scattering when the band edge occurs at a number of equivalent points in momentum space (Herring 1955), or a non parabolic profile of the band (Radcliffe 1955), and others. When inter-valley scattering is important, the relaxation time becomes a tensor (Herring and Vogt 1956).

The position is less satisfactory at low temperatures where impurity scattering predominates, as no law of temperature variation has been clearly established. Undoubtedly the mobility at ordinary temperature decreases with increasing impurity content, but even this is established only qualitatively. The difficulty is that the impurity content cannot

be taken as equal to the residual amount of carriers at low temperatures, because of the possibility of a high degree of compensation between donors and acceptors. This question of the temperature variation of mobility in the impurity region must be left open until crystals with known amount of impurities are available.

Studies of changes of resistance in a magnetic field, of the Nernst effect and of minor thermomagnetic effects may bring additional information on mobilities, but no effective method of using these data has yet been devised. In all these experiments one determines the mobility of majority carriers, or the ambipolar mobility in intrinsic samples. The mobility of the minority carriers, in the absence of drift experiments, has been measured only by means of the dependence on magnetic field of the photo-electromagnetic effect (see e.g. Pincherle 1955 a). For instance in n-samples the magnitude of this effect is proportional to $\mu_h B (1 + \mu_h^2 B^2)^{-1/2}$. The method is not very accurate because, except when the mobility is high, the fields required for a reliable determination are very strong.

§ 4. THE III-V COMPOUNDS

4.1. General Considerations

This is at present the most promising group of S.I.C. Though, as so many brothers, they have a general family likeness, for instance they all crystallize in the zincblende structure, there are, as among brothers, individual characteristics and peculiarities.

There have been several attempts to understand their properties on the basis of semi-empirical theories and simple models. Mention has already been made in § 3.3 of Goodman's speculations and of Seraphin's one dimensional treatment; and Herman (1955) has published an account of some interesting qualitative studies of the band structure of these compounds, using perturbation theory on the band structure of the elements of Group IV. Further qualitative results have been obtained from a study of a hypothetical diatomic molecule with charges $(1+\epsilon)$ and $(1-\epsilon)$ on the two atoms (Heywang and Seraphin 1956). A variational treatment shows that, when ϵ increases, the binding becomes stronger and the ground state becomes more widely separated from the excited states, whereas the distance of equilibrium does not change much. This calculation thus justifies the statement that in a crystal both the melting point and the energy gap increase with the degree of ionicity.

However, it does not seem likely that properties of the crystal such as the energy gap and the effective mass tensors are determined by factors which can be discussed in a simple way. This conclusion is supported by the example of the Group IV elements. The minima of the conduction band in Si lie along the axes equivalent to (1,0,0), while in Ge they lie along axes equivalent to (1,1,1). Such a result could only be obtained by

a detailed calculation of the band structure. Calculations of this type on S.I.C. are now in progress (Howarth, private communication). As already remarked, completely self-consistent calculations are beyond the capacity even of electronic computers, and it is necessary to make some hypothesis on the charge distribution in the unit cell, that is to say it is necessary to decide on the type of bonding which is dominant in the crystal. Slater and Koster (1954) have given an illuminating theoretical treatment of this question (see also Krebs 1954). There are a few experimental data which are relevant to deciding the nature of the bond. One is the observation by Pfister (1955) that InSb and AlSb cleave along the (1,1,0) direction, like ZnS, and not along the (1,1,1) direction, as Ge does. This indicates an electrostatic attraction between planes perpendicular to the (1,1,1) direction. Again, the strong lattice absorption band at 52μ observed by Spitzer and Fan (1955) is evidence for the existence of a dipole moment in the unit cell. It has been suggested by Birman (private communication) that the bond dipole moment might be estimated from the piezoelectric coefficient. Such a dipole would give a contribution to the refractive index which might be detected by comparing the value of the index at low frequencies and in the infra-red.

In principle the charge density in the unit cell can be calculated from the intensity of the lines in the x-ray diffraction pattern. In particular, certain lines which are forbidden by the additional symmetry of the diamond lattice can occur with a zincblende structure. Such an extra line has been observed in a powder photograph of GaSb (Rennie, private communication). These lines are of course related to the splitting of some degeneracies in the band structure which will be discussed below.

Some general theoretical work has been completed on the symmetry properties of the energy bands for zincblende type crystals. Bell (1954) has applied the methods of group theory to a classification of the various bands and this work has been extended independently by Dresselhaus (1955) and by Parmenter (1955) to include spin-orbit coupling which is of fundamental importance in these substances. Herman (1955) has used these results to determine which energy contours are possible at the band edge. He finds that, if the edge is at $k=0$ (conduction band of InSb), the constant energy surfaces consist of two nearly spherical sheets, in contact with each other at the origin and along the (1,0,0), (1,1,0) and (1,1,1) directions, but distinct in intermediate directions. A band edge may occur alternatively at the twenty-four corners of the truncated octahedron which constitutes the elementary cell in momentum space for zincblende type crystals. In this case, in the reduced zone scheme the equienergy surfaces consist of six ellipsoids; the mass tensor contains three different effective masses. Herman suggests that this may be the state of affairs for the valence band of InSb. Another possibility is that the maxima lie at a set of equivalent points in the neighbourhood of one of the sets of principal axes. There may be, for instance, 48 ellipsoids arranged in six clusters of eight around the (1,0,0)-axes. In a diatomic

substance, spin-orbit coupling will always shift the minima off these axes.

Herman speculated further on the band structure of the III-V compounds and attempted to deduce it by perturbation methods from the more or less known band structure of diamond type substances. It is an experimental fact that the lattice constant of GaAs, and also of the II-VI and I-VII compounds ZnSe and CuBr from elements of the same row of the periodic Table, is very nearly the same as that of the element of Group IV, Ge, and the same happens for the homologous compounds in the other rows of the periodic Table, while compounds such as GaSb may be taken to have very nearly the same lattice constant as a hypothetical GeSn. This being so, the Hamiltonian describing the intermetallic compound is exactly that for the Group IV element plus the potential due to a lattice of positive and negative charges on alternate sites (charge e for the III-V, $2e$ for the II-VI compound, etc.). This potential, which is odd with respect to inversion through the mid-point of any line joining nearest neighbours, was treated as a perturbation applied to the states of Group IV elements whose wave functions had been calculated previously by Herman himself and by others. The perturbation removes some degeneracies, for instance those at the centres of the square faces of the truncated octahedron. Otherwise the quantitative effect is small, and the general features of the band structure are expected to remain, but the various minima of the energy at different points in momentum space are influenced in different measure. Thus a stationary point for the valence band of Ge at the corners of the reduced zone may become the absolute maximum of the valence band of GaAs. By a judicious combination of the results of this calculation and of experimental observations, Herman makes plausible guesses of the detailed band structure of several of the III-V compounds.

Evidence on whether the band edge remains essentially in the same position in momentum space in passing from one compound to another, or whether it shifts to a different position, may be obtained from a study of the energy gap of mixed crystals as a function of composition. If the edge shifts to a different position, a discontinuity of the rate of change of the energy gap is produced. Folberth (1955) finds that in mixed crystals of InAs and InP, E_g varies linearly with composition, whereas for GaAs-GaP the variation is slow near GaP but steepens towards GaAs. From the results one cannot however say that there is a definite break in the slope. For the system InAs-InP also the electron Hall mobility at room temperature varies smoothly with composition from the value 20 000 cm²/voltsec in InAs to 3000 in InP. This may indicate that impurity scattering was already large even in the 100% crystals.

Qualitative results on the band structure of compounds crystallizing in the zincblende lattice have also been obtained by Slater and Koster (1954) from application of a simplified LCAO method. As in the well-known diamond structure, there are in a zincblende structure eight bands

arising from the s and p orbitals of the two atoms in the unit cell. At $\mathbf{k}=0$ two bands are of the non-degenerate s-type, and two are threefold degenerate p-type. As for the diamond structure, the lower set of bands is capable of holding eight electrons per unit cell, forming the valence band, and the upper set, forming the conduction band, can hold the same number. d-type bands are likely to overlap the valence band for compounds of the heavier elements. The difference in symmetry between the ZnS structure and the diamond structure introduces only minor qualitative differences, provided the spin-orbit coupling is neglected. At first sight, a problem seems to be presented in, say, InSb, by the fact that, the atoms presumably being almost neutral, we have five electrons in the average around the Sb atom and three about the In atom. And yet the band structure is qualitatively the same as in Ge and the charge density has the same sort of symmetry which would be produced by sp_3 orbitals. One of the interesting results of Slater and Koster's calculation is to show how, by expressing the wave functions as linear combinations of atomic orbitals, it is possible to arrive at the characteristics of a closed shell of electrons with any total charge, even fractionary on the In and Sb atoms. This discussion throws much light on the relative importance of the two extreme configurations which can be envisaged. In one InSb is made up of In^- and Sb^+ , each with four outer electrons and forming covalent bonds; in the other, of In^{3+} and Sb^{3-} , each with closed shells and forming ionic bonds. The structure resonates between these two, but the covalent picture is the better, as indicated by the crystal structure. However, owing to the potential well about the Sb atom being deeper than that about the In atom, there is, for the occupied states, more charge about the Sb atom (the converse applies to the unoccupied states), i.e. the wave function at $\mathbf{k}=0$ contains a larger fraction of that unperturbed wave function whose diagonal energy is lower (Sb) than of that whose diagonal energy is higher (In).

The question of bond relationships in diamond-type semiconductors has been further discussed by Goodman and Douglas (1954) and by Goodman (1955), mainly on the basis of the concept of electronegativity. They observe that the greater mean electronic density in the neighbourhood of the more electronegative atom is equivalent to an ionic term in the bonding, and, as discussed in § 3.3, correlate the bond dipole with the carrier mobility.

4.2. Aluminium Antimonide

The following references refer to this substance

- Blunt *et al.* (1954 a) : preparation; R , σ versus T ; optical absorption.
- Breckenridge *et al.* (1954 b) : preparation; R , σ versus T ; optical absorption.
- Cunnell *et al.* (1954) : infra-red transmission.
- Gremmelmaier and Madelung (1953) : preparation.
- Justi and Lautz (1953) : preparation; x-ray; R , σ versus T ; rectification.
- Köster and Thoma (1955) : mixed crystals with GaSb and InSb.
- Oswald and Schade (1954) : optical absorption.

Pfister (1955): cleaving properties.

Sasaki *et al.* (1954): preparation; R , σ , TEP versus T .

Schell (1956): zone-refining.

Welker (1952, 1953): preparation; x-ray; R , σ versus T ; rectification theory.

Welker (1954): general review.

In the aluminium compounds the ionic component of the bond ought to be smaller than in the other III-V semiconductors since the radius of the Al^{3+} ion is small. Hence the lattice vibrations would have greater amplitude and the mobility would be lower.

AlSb is the only III-V compound containing Al which has been at all investigated. AlN crystallizes in the wurtzite structure, has a very high melting point and is an insulator (Friederich 1925). AlP and AlAs (Natta and Passerini 1928 a), with the zincblende structure, are difficult to prepare, unstable and very brittle. AlSb is also rather unstable and decomposes in humid air. Its density is 4.25. It is prepared by melting the elements together and can be zone refined†. Crystals have been pulled by the Kyropoulos technique (for details of this technique see Teal and Little 1950). When first prepared AlSb is always p-type, but can be made n-type by doping with Te. Lead is said to be the main impurity. The highest resistivity samples which have been produced showed a carrier density of the order of 10^{15} cm^{-3} .

E_g is 1.60 eV at the absolute zero and 1.52 at room temperature. The main absorption edge is not well defined. Several impurity absorption bands and activation energies have been observed, the most prominent being at 0.08 and 0.53 eV. Some of these absorptions may be due to intraband transitions as in p-type Ge. Mobilities are not known with any accuracy; they appear to be low, and it has been reported that holes are more mobile than electrons. Some evidence for the $T^{-3/2}$ law has been found. A hole effective mass of $(1.8 \pm 0.8)m$ has been reported, from TEP measurements. The apparent high value may be due to degeneracy of the band edge (existence of a number of equivalent energy minima).

AlSb is a good rectifier: rectification ratios up to 10^4 have been reported, and it can stand back voltages of 300 volt.

4.3. Gallium Phosphide

Folberth (1955): mixed crystals with GaAs.

Folberth and Oswald (1954): preparation; optical absorption; R , σ versus T ; photoelectricity; rectification.

Oswald (1955): optical and infra-red absorption.

Welker (1955): general review.

Wolff *et al.* (1955): electroluminescence.

The compound is produced by heating gallium hydroxide in hydrogen saturated with P vapour at 500°C . Crystals have been grown: they are orange in colour and transparent. The energy gap is 2.4 eV at 0°K

† For details of the zone-refining technique see Pfann (1952).

and decreases rather rapidly with increasing T reaching about 2.25 at room temperature. The annealed crystals were p-type. n-type specimens could be produced by doping with S. GaP shows rectification at point contacts and photoconduction. The infra-red absorption presents a complicated structure near 14μ , possibly due to lattice absorption. Electro-luminescence has been observed in this substance.

4.4. Gallium Arsenide

- Barrie *et al.* (1954): preparation; R , σ versus T ; TEP; rectification.
 Braunstein (1955): recombination radiation.
 Cunnell *et al.* (1954): infra-red transmission.
 Folberth (1955): mixed crystals with GaP.
 Folberth and Weiss (1955): electrical properties.
 Gans *et al.* (1953): preparation; rectification; photoconduction.
 Gremmelmaier (1955): use in a solar battery.
 Gremmelmaier (1956): production of single crystals.
 Herman (1955): band structure.
 Hrostowski and Tanenbaum (1954): preparation; optical absorption; R , σ versus T ; magnetoresistance.
 Jenny *et al.* (1956): use in a solar battery.
 Oswald (1955): optical absorption.
 Oswald and Schade (1954): optical properties.
 Pfister (1956): photoeffect produced by x-rays on p-n junction.
 Welker (1952, 1953): preparation; x-ray; R , σ versus T ; rectification; theory.
 Welker (1954): general review.
 Welker (1955): general review.

Like the other arsenides, the compound is prepared reacting the components in sealed silica tubes at high temperature. It decomposes at the melting point, and this fact prevents its being zone refined; otherwise is stable. Small single crystals have been produced by pulling technique. They were generally n-type with electron densities of 10^{16} – 10^{18} cm $^{-3}$, this density remaining practically constant from 4 to 400°K. Mixed crystals with GaP in all proportions have been produced, the lattice parameter and the energy gap varying monotonically; the variation of the energy gap is however steeper near 100% GaAs.

Electrical and optical measurements agree that the energy gap is about 1.5 eV at 0°K and 1.35 at room temperature showing the relatively large shift of $-(5-6) \times 10^{-4}$ eV/degree. However the cut-off of photoconductivity is at 1.13 eV, and the peak of the recombination radiation produced by carrier injection at room temperature lies at 1.10 eV. At 77°K this peak is at 1.19. The tail of this radiation extends at both temperatures to 0.7–0.8 eV. No theory has yet been given of the shape and width of the recombination line. From the ratio of number of photons emitted to number of minority carriers injected, a lifetime of added carriers of the order of 10^{-8} sec may be estimated.

The electron mobility at 700°C is 1100 cm 2 /voltsec. Application of the $T^{-3/2}$ law gives values of the order of 7000 at room temperature.

The highest observed value is 4000. The mobility ratio is given as 10 by the sign reversal of the Hall effect in p-type specimens. The refractive index is 3.3–3.4. Thermoelectric power measurements of n-samples combined with electrical and optical data lead to an electron effective mass of (0.024–0.032) m . According to Herman, the band structure of GaAs would be very similar to that of Ge (Ga and As are the two elements immediately preceding and following Ge in the periodic Table), apart from removal of degeneracies. The behaviour of the Hall coefficient in the extrinsic range is somewhat anomalous since it does not stay constant, as in all the other compounds.

GaAs is a good point contact rectifier and a good photodetector. The free carrier absorption, in n-samples, obeys the λ^2 law. Its energy gap, slightly larger than that of Si, and thus nearer to the wavelength of maximum solar emission, makes it suitable in principle for the construction of a solar battery (in which solar energy is directly converted into electrical energy through the photovoltaic effect at a p–n junction). The efficiency reached up to now is only 6.5%, but there is no reason why, with the availability of better material, it may not be considerably improved. The photoeffect produced by x-rays on a p–n junction of GaAs has been suggested as a suitable method for the dosage of x-rays.

4.5. Gallium Antimonide

Blunt *et al.* (1954 b) : R , σ versus T ; optical absorption.

Braunstein (1955) : recombination radiation.

Breckenridge *et al.* (1954 b) : preparation ; doping ; optical properties ; R , σ versus T .

Cleland and Crawford (1955) : fast neutron bombardment.

Cunnell *et al.* (1954) : infra-red transmission.

Detwiler (1955) : R , σ versus T ; p–n junctions ; preparation ; doping.

Hrostowski and Tanenbaum (1954) : preparation ; R , σ versus T ; magnetic resonance.

Leifer and Dunlap (1954) : R , σ versus T for p-samples ; optical absorption.

Long (1956) : effect of pressure on electrical properties.

Mokrovskii and Regel (1952) : density and conductivity at melting point.

Oswald and Schade (1954) : optical properties.

Roberts and Quarrington (1955) : optical properties.

Shulman *et al.* (1955) : nuclear magnetic resonance.

Welker (1953) : R , σ versus T ; rectification ; theory.

Welker (1954) : general review.

GaSb has been prepared by melting together the components, generally in the boat of the zone refining apparatus, under hydrogen. It is very stable. Crystals may be pulled with the Kyropoulos technique. When first prepared it is always p-type, but may be made n by doping with Te. The purest specimens obtained had a carrier concentration of about 10^{17} cm^{-3} . A large increase of density is observed at the melting point, where also the conductivity increases.

Electrical and optical experiments agree in giving the energy gap at about 0.78 eV at 0°K and 0.70 at room temperature. The absorption edge is very steep. The peak of the recombination radiation is at 0.625

and its tail ends at 0.53 (at room temperature). In p-type specimens an impurity activation energy of 0.025 eV has been observed. The mobility is not so high as might perhaps have been expected on the rule that it increases with increasing atomic weight of the components: probably it is not higher than in GaAs. At room temperature electron mobilities up to 5000 cm²/voltsec have been reported, and hole mobilities up to 1000. In contrast to what happens in the other compounds, the electron mobility of GaSb is independent of pressure. The mobility ratio is given as 5 also by the sign reversal of the Hall effect in p-type specimens. Above room temperature the hole mobility follows approximately the $T^{-3/2}$ law, while below room temperature a $T^{0.87}$ law has been reported, probably reflecting the onset of impurity scattering.

Under fast neutron irradiation the carrier concentration of both p and n polycrystalline samples is decreased; shallow traps are produced. There is evidence that vacant lattice sites as well as interstitial atoms are formed. The mobility is also decreased.

GaSb is not a good rectifier. A p-n junction has been grown and from its characteristics the value 0.78 eV has been deduced for E_G , in agreement with the other determinations. From a combination of electrical and optical experiments effective masses of 0.2 m for electrons and 0.4 m for holes have been estimated. If these values are confirmed, the electron effective mass too is 'out of step' with those of the homologous compounds.

Magnetoresistance data indicate spherical energy surfaces at the bottom of the conduction band. On the other hand a study of the optical absorption edge shows that the interband transition is not optically allowed, so that the top of the valence band is not at $\mathbf{k}=0$. The band structure may thus be similar to that of InSb discussed in §4.8; on the other hand, as remarked above, there are several respects under which GaSb shows an individual behaviour.

4.6. Indium Phosphide

- Braunstein (1955): recombination radiation.
- Cunnell *et al.* (1954): infra-red transmission.
- Folberth (1955): mixed crystals with InAs.
- Folberth and Weiss (1955): preparation; R , σ versus T .
- Gremmelmaier and Welker (1956): application as a neutron detector.
- Iandelli (1941): preparation; x-ray.
- Oswald (1955): optical and infra-red absorption.
- Oswald and Schade (1954): optical properties.
- Weiss (1956 b): mixed crystals with InAs.
- Welker (1952, 1953): optical and electrical properties; theory.
- Welker (1954): general review.
- Welker (1955): general review.

InP has been prepared in sealed tubes under controlled conditions, and zone refined. In contrast to other compounds, it tends to become n-type on zone melting. It can then be made p-type by doping with Zn. Polycrystalline samples only have been prepared. From R and σ measurements the energy gap at 0°K is 1.34 eV. The highest electron mobility

measured at room temperature was 3400, but, since the sample showed the $T^{-3/2}$ law only at higher temperatures, it was argued that in purer samples μ_e should be at least 5000. The hole mobility is much smaller and the Hall coefficient curves for p-type specimens present the characteristics associated with a high mobility ratio.

The optical energy gap is $1.42\text{--}4.7 \times 10^{-4}$ T ev. Combining this value with the electrical data, one obtains $m_c = (m_e^+ m_h^+)^{1/2} = 0.23 m$. The infra-red absorption spectrum shows a band at 15μ , probably due to the lattice. Otherwise the infra-red absorption of InP is very low, lower than that of the purest samples of Ge.

In mixed crystals of InP and InAs the energy gap varies linearly with composition. The mobilities vary monotonically, and their temperature dependence is independent of composition. These results indicate that the band structure must be the same in the two substances.

InP is a good rectifier and a transistor effect has been reported. It would appear however that only voltage, and not power amplification was obtained. p-n junctions may be grown and their use for neutron detection has been suggested; irradiation by neutrons produces several radioactive isotopes of In and the extra current across the junction due to the electron-hole pairs produced by the ionizing particles emitted by these isotopes decays with the corresponding periods.

4.7. Indium Arsenide

- Cunnell *et al.* (1954): infra-red transmission.
 Folberth *et al.* (1953): electrical properties.
 Folberth *et al.* (1954): doping; R , σ versus T .
 Folberth (1955): mixed crystals with InP.
 Gans *et al.* (1953): preparation; rectification; photoconductivity.
 Gremmelmaier (1956): production of single crystals.
 Hrostowski and Tanenbaum (1954): R , σ versus T ; optical absorption; magnetic resonance.
 Hrostowski *et al.* (1954): shift of absorption edge with n .
 Iandelli (1941): preparation; x-ray.
 Long (1956): effect of pressure on electrical properties.
 Oswald and Schade (1954): optical properties.
 Schillmann (1956 a, b): effect and diffusion of impurity atoms.
 Shih and Peretti (1953): mixed crystals with InSb.
 Stern and Talley (1955): theory of energy levels of impurities.
 Talley and Enright (1954): photovoltaic effect.
 Talley and Stern (1955): theory of energy levels of impurities.
 Taylor (1955): pressure effects.
 Weiss (1956 a): effective masses from TEP.
 Weiss (1956 b): mixed crystals with InP.
 Welker (1954): general review.

InAs is prepared by reacting the components in a sealed quartz tube at high temperature under controlled conditions. It decomposes at the melting point, but is otherwise stable. Crystals may be produced by the pulling technique. Best purity achieved so far is of the order of 10^{15} carriers cm^{-3} . Mixed crystals with InP have also been grown. When foreign atoms are introduced into InAs it is found that the elements of Groups II and IV substitute In, the former acting as acceptors, the

latter as donors. The elements of Group VI substitute As and act as donors. The ionization energy of all these impurities is very small (<0.005). Their introduction causes a decrease of carrier mobility which is independent of the nature of the foreign atom, at a given concentration. If acceptors diffuse into n-type material, a p-n junction is formed and by measuring its motion it is possible to determine the activation energies for diffusion and the diffusion coefficients of the various foreign atoms. The activation energies are 2.2 eV for substitutes of As (except Te for which the activation energy is 1.28), and 1.17 eV for substitutes of In. The diffusion coefficients at 900°C are found to lie between 10^{-11} and 10^{-8} cm² sec⁻¹.

In view of the high electron mobility, the energy gap at 0°K obtained from the electrical data is not reliable. It is given as 0.47 ± 0.02 eV. Optical experiments give $E_g = 0.33$ at room temperature. However the cut-off of a photovoltaic cell made out of a p-n junction was about 0.27 at 77°K. E_g increases with increasing pressure at the rate of $5.5 \cdot 10^{-6}$ eV/atmos. InAs shows the Burstein-Moss effect, though to a lesser degree than InSb: the absorption edge shifts by about 0.7μ for 10^{19} electrons cm⁻³. This effect may perhaps explain the anomalous value of E_g obtained with the photocell, as shown in a theoretical analysis of Talley and Stern (1955). They treated the energy levels of ordered donor impurities by the cellular method using hydrogen-like potentials, and found that the band of impurity levels becomes wider with increasing N (density of impurity centres), eventually overlapping with the bottom of the conduction band; this would occur in InAs for N of the order 1.5×10^{16} . If the bands overlap, and if the electrons are then removed from these bands by a comparable number of acceptors, the edge may be shifted to energies lower than for intrinsic material. Experimental results using variously doped materials appear to support this theory. The presence of the impurity band will also affect the electrical properties. The impurities will not generally form an ordered array, but will be distributed at random. It is known (Aigrain 1954) that in this case the impurity band is broader and has a tail towards high energies.

The ratio of electron to hole mobility is very large, the electron mobility being greater than 15 000 at room temperature, while hole mobilities have been estimated only from the sign reversal of the Hall effect and found to be no larger than 200. At high temperatures μ_e follows the $T^{-3/2}$ law and extrapolation by means of such law leads to room temperature mobilities of 30 000. The hole mobility, as far as can be ascertained, decreases more rapidly with increasing temperature, the exponent being greater than 2. This fact may point to the existence of a number of equivalent maxima at the top of the valence band. The electron mobility varies appreciably with pressure decreasing by about 7% at 2000 atmos.

From a combination of electrical and optical experiments, $m_e = (m_e^+ m_h^+)^{1/2} = 0.10 m$. Cyclotron resonance experiments have been

attempted but without success. From TEP measurements between 500 and 800°K, $m_e^+ = 0.064 m$, $m_h^+ = 0.33 m$. The small ionization energy of impurity atoms would indicate lower values.

As already mentioned, a p-n junction has been grown, which showed a good photovoltaic effect. The time constant of this cell was 7 μ sec.

4.8. Indium Antimonide

- Aigrain and des Cloiseaux (1955): theory of energy levels of impurities.
 Aigrain *et al.* (1956): thermomagnetolectric effects.
 Allen and Mackintosh (1955): implications of small E_G and m^+ .
 Austin and McClymont (1954): optical properties; R , σ versus T ; analysis of data.
 Avery and Jenkins (1955): lifetime of added carriers; radiation recombination.
 Avery *et al.* (1954): optical and photoelectric properties.
 Barlow (1955): amplifier based on Hall effect.
 Barrie and Edmond (1955): optical absorption; R , σ , TEP as function of impurity concentration; density of states in conduction band.
 Blount *et al.* (1956): interpretation of absorption edge.
 Breckenridge *et al.* (1954 a, b): optical absorption; R , σ versus T .
 Burstein (1954): theory of shift of absorption edge with donor concentration.
 Busch *et al.* (1955): self-Hall effect.
 Busch and Schneider (1954 a, b): thermal conductivity.
 Busch and Vogt (1954): electric and magnetic properties at melting point.
 Busch and Winkler (1953 a): x-ray data; R , σ versus T .
 Cleland and Crawford (1954): radiation effects.
 Cunnell *et al.* (1953): preparation, R , σ versus T .
 Cunnell *et al.* (1954): infra-red transmission.
 De Vaux and Pizzarello (1956): elastic constants.
 Dresselhaus *et al.* (1955 a): cyclotron resonances.
 Dresselhaus *et al.* (1955 b): plasma resonance.
 Folberth and Madelung (1953): theoretical interpretation of σ versus T curves.
 Frederikse and Blunt (1955): optical absorption; photoconductivity, photovoltaic, PEM effects.
 Frederikse and Mielczarek (1955): thermoelectric power.
 Fritzsche and Lark-Horowitz (1955): R , σ , magnetoresistance of p-samples at liquid He temperatures.
 Fröhlich and Kittel (1954): theory of thermal conductivity.
 Gielessen and von Klitzing (1956): effect of pressure on R , σ , magnetoresistance.
 Goodwin and McLean (1956): radiative lifetime.
 Gremmelmaier and Madelung (1953): preparation.
 Harman (1956): purification; zone-refining.
 Harman *et al.* (1954): R and magnetoresistance of p-samples; theoretical interpretation.
 Harman *et al.* (1955): zone-refining.
 Harrison (1956): piezoelectricity as a source of carrier scattering.
 Hartell (1954): application as a power meter.
 Hatton and Rollin (1954): R , σ , magnetoresistance of p-samples at liquid He.
 Herman (1955): band structure.
 Hilsun *et al.* (1955): photoelectromagnetic effect.
 Howarth *et al.* (1956): variation of R with B in p-samples.
 Hrostowski and Tanenbaum (1954): preparation; optical absorption; R , σ versus T ; magnetoresistance.
 Hrostowski *et al.* (1954): optical absorption of n-samples.

- Hrostowski *et al.* (1955) : R , σ versus T down to 1.3°K ; variation of R with B .
 Iandelli (1941) : preparation ; x-ray.
 Kaiser and Fan (1955) : infra-red absorption.
 Kanai (1955) : magnetoresistance of impure n-samples.
 Keyes (1955) : effect of pressure on conductivity.
 Köster and Thoma (1955) : mixed crystals with AlSb and GaSb.
 Kuhrt (1954) : Hall generator.
 Kuhrt and Braunersreuther (1954) : application of Hall generator.
 Kurnick and Zitter (1956) : photoconductivity and PEM efficiency ; theoretical treatment.
 Kurnick *et al.* (1954) : photoconductivity and PEM effects ; lifetimes.
 Kurnick *et al.* (1955) : p-n junctions ; photoconductivity ; lifetimes.
 Long (1955) : effect of pressure on R and σ .
 Long (1956) : variation of R , σ , magnetoresistance with pressure.
 Mackintosh (1956) : explanation of negative magnetoresistance.
 Mackintosh and Allen (1955) : calculation of radiation recombination lifetime.
 Madelung (1953) : theory of magnetoresistance in high fields.
 Madelung and Weiss (1954) : R , σ versus T .
 Mansfield (1955) : magnetoresistance of degenerate samples.
 Millea and Tomizuka (1956) : melting patterns.
 Mitchell *et al.* (1955) : photovoltaic cell.
 Mokrovskii and Regel (1952) : density and conduction at melting point.
 Moss (1954) : theory of shift of absorption edge with donor concentration.
 Moss (1955) : bulk and surface lifetimes from photovoltaic and photoconductive effects.
 Oswald and Schade (1954) : optical properties.
 Pearson and Tanenbaum (1953) : magnetoresistance.
 Pfister (1955) : cleaving properties.
 Price (1955) : theory of anomalous thermal conductivity.
 Rickayzen (1955) : hydrogen approximation for impurity levels.
 Roberts and Quarrington (1955) : optical absorption.
 Rollin and Petford (1955) : R , σ , magnetoresistance at liquid He temperature.
 Ross and Saker (1955) : application in various devices.
 Ross and Thompson (1955) : amplifier based on Hall effect.
 Saker *et al.* (1955) : application as a fluxmeter.
 Shih and Peretti (1953) : mixed crystals with InAs.
 Shulman *et al.* (1955) : nuclear magnetic resonance.
 Slater and Koster (1954) : tight binding theory of band structure.
 Spitzer and Fan (1955) : infra-red absorption.
 Stern and Talley (1955) : theory of energy levels of impurities.
 Stevens and Crawford (1955) : magnetic susceptibility.
 Tanenbaum and Briggs (1953) : optical absorption.
 Tanenbaum and Maita (1953) : R , σ versus T .
 Tauc and Abraham (1954) : photoconductivity.
 Tauc and Matyas (1955) : TEP ; R , σ versus T .
 Tauc *et al.* (1954) : photoconductivity.
 Thuillier (1955) : theory of thermal conductivity.
 Weiss (1953) : R , σ versus T ; magnetoresistance.
 Weiss (1956 a) : effective masses from TEP.
 Weiss and Welker (1954) : dependence of magnetoresistance on shape.
 Welker (1952, 1953) : preparation ; x-ray ; R , σ versus T ; rectification ; theory.
 Welker (1954, 1956) : general review.
 Yoshinaga (1955) : reflectivity in the infra-red.
 Yoshinaga and Oetjen (1956) : optical properties in the far infra-red.

As the length of the list of references shows, InSb is by far the best studied of all intermetallic compounds. Among the striking properties which have attracted so much attention to this substance we may mention : the very high electron mobility, which magnifies all magnetic effects permitting novel applications, such as the use of the Hall effect for power amplification ; the small energy gap, which makes it suitable for radiation detection in the infra-red through the photovoltaic, photoconductive, or photoelectromagnetic effects ; its almost complete degeneracy (in n-samples) at all temperatures due to the exceedingly small value of the electron effective mass ; the fact, due to the same cause, that the conduction band can, in impure samples, be filled up to an appreciable level with electron to cause a shift of the absorption edge (Burstein-Moss effect).

InSb is easily formed by direct reaction of the two elements and is very stable. Its density is 5.7 and, as with Ge, the density and conductivity increase when the substance melts. As for the homologous compounds, the solubility of the elements in the compound is very small, so that almost perfect stoichiometry is reached automatically. Densities of impurity carriers as low as 10^{13} cm^{-3} have been reported ; however the carrier density does not necessarily equal the impurity concentration, since there may be a high degree of compensation between donors and acceptors.

Harman *et al.* (1955), Harman (1956) have described experiments on the zone refining of ingots of InSb which were initially p-type (according to the sign of the TEP). After about 30 passes of a zone 2–2.5 cm wide, five characteristic regions could be distinguished along the ingot. From the 'pure' to the 'impure' end they were : (1) an n-type region along which the concentration decreased and the mobility increased ; (2) an n-type region along which both the concentration and the mobility were decreasing ; (3) an inhomogeneous region of mixed conduction ; (4) a p-type region in which the concentration and the mobility were low ; (5) a p-type region along which the concentration was increasing. In two ingots made from In which had been purified by electrodeposition and by zone-melting, electron concentrations of 10^{16} and $2 \times 10^{15} \text{ cm}^{-3}$ respectively were observed at the beginning of region (1). These values dropped to about 3×10^{14} and 10^{14} respectively in region (3). The hole concentration was about 4×10^{14} in region (3) rising to 9×10^{16} in region (5). The main acceptor impurity was identified as Zn, which raises the melting point of InSb. The most slowly segregating impurity was Te which is a donor and lowers the melting point. Harman *et al.* also made an experiment on the effectiveness of zone-refining in a sample doped with Zn. The original specimen was estimated to have 10^{16} cm^{-3} total carrier concentration and was doped with $2.6 \times 10^{18} \text{ cm}^{-3}$ Zn atoms. After zone-levelling the carrier concentration was more or less uniform and equal to the density of the doping atoms. After five zone passes at 9 cm/hour the concentration was 1.5×10^{17} at one end and 10^{19} at the other.

Having purified the material, single crystals are then pulled. This is generally done in silica crucibles in hydrogen. Very accurate control of the temperature is necessary to obtain good crystals.

Energy gap. The energy gap has been determined accurately between absolute zero and room temperature from optical absorption and photoconductivity data. The edge is so steep, that the particular rule chosen to define it hardly affects the second decimal figure. E_G is 0.23 eV at absolute zero, remains at this value almost up to liquid air temperature, and then decreases almost linearly with increasing T reaching 0.17 at room temperature. The gap increases with pressure at the rate of 1.5×10^{-5} eV per kg/cm². The thermal energy gap cannot be derived simply from the usual curves on account of the very high mobility ratio, as discussed in § 2.3. Application of the simple formulae by the early experimenters had led to values of E_G around 0.4–0.5 eV.

Burstein-Moss effect. Several experimenters agree that the energy gap increases to about 0.4 eV when 4×10^{18} electrons/cm³ occupy the conduction band. With simple assumptions on the shape of the band one can, from these data, deduce the value 0.028 for the electron effective mass. However the effect becomes measurable at lower concentrations than are compatible with this value of the mass, and the effect at these lower concentrations indicates an effective mass near to 0.01, in agreement with cyclotron resonance results. It is of course plausible that the effective mass should increase higher up in the band. Evidence for this was found from a combination of optical and electrical experiments on samples of increasing impurity content: they showed that the conduction band is not parabolic and may perhaps be fitted by an expression

$$E = ak^2(1 - bk^2).$$

The optical results could be explained assuming that the band is filled up to above the point of inflection. However, not all the remaining data could be fitted into this scheme (Barrie and Edmund 1955).

The analysis carried out by Talley and Stern for the case of InAs applies also to InSb. The effective electron mass required to fit experimental data is 0.03 m . A similar calculation, using second order perturbation theory, has been carried out by Aigrain and des Cloizeaux (1955). In any analysis of the conduction band one should remember that at some, as yet unknown, donor density it will have merged with the impurity band.

Carrier mobilities. The mobilities have been calculated from the Hall effect and conductivity data and from the magnetoresistance. The highest values obtained at room temperature are 80 000 cm²/voltsec for electrons and 4000 for holes (though the sign reversal of the Hall effect leads in most samples to values of the mobility ratio higher than 20). Weiss (1953) found that the two types of measurements gave different results. It is very important that the experiments be done at such low fields that the perturbation theory of these effects is valid. Harman *et al.* (1954), however, found that the standard theory was able to account satisfactorily for the following facts in p-type samples: that when the field is increased the zero and minimum of the Hall coefficient occur at

higher temperatures ; that the maximum in the magnetoresistance occurs at a higher temperature ; that the minimum of the Hall coefficient becomes smaller in absolute value ; and that at all fields the maximum in the magnetoresistance occurs at about the same temperature as the maximum of the Hall coefficient. It is noteworthy that the corresponding effects in p-type Ge cannot be understood on the basis of a simple theory. Howarth *et al.* (1956) found that the dependence of R on B for p specimens is marked only in the region of mixed conduction and that standard theory fitted their experimental results. From such a study it is possible to obtain the intrinsic carrier concentration at lower temperatures than with other methods (e.g. down to 165°K for a specimen with 4×10^{15} extrinsic holes cm^{-3}).

The temperature variation of the electron mobility is easier to measure than that of the hole mobility because the mobility ratio is so large and the electron mobility practically coincides with the intrinsic mobility. It is reported to vary as $T^{-1.63}$ in the temperature range where lattice scattering predominates, as does the mobility of electrons in Ge. The mobility at room temperature is often found to rise after the crystal has been annealed, suggesting that there is normally a good deal of scattering by lattice defects at this temperature. The lattice scattering mobility of holes has been reported to vary as $T^{-2.1}$ (Hrostowski *et al.* 1955). The exponent larger than 1.5 is consistent with a number of equivalent energy maxima in the valence band. There is considerable scatter among the values of the mobility ratio observed in different samples and at different temperatures. Howarth *et al.* (1956) ascribe this scatter to a difference in the importance of impurity scattering of electrons and holes respectively, a fact to be expected according to the theory of impurity scattering in view of the difference in effective masses. Values as high as $b=85$ have been reported (Tanenbaum and Maita 1953).

The electron mobility is found to decrease with increasing pressure, being approximately inversely proportional to the gap. According to Long (1955) the effect is due to an increase in effective mass as the bands move apart. Keyes (1955) suggests that the effect may be due to a change in the rate of electron-hole collisions. The hole mobility is independent of pressure however.

Since InSb is piezoelectric, there will be an electric polarization associated with the acoustical modes of vibration. The corresponding periodic potential will contribute to the scattering of carriers. The relaxation time for this process is inversely proportional to the square of the piezoelectric constant and appears to be too long to be of practical importance (Harrison 1956). In non degenerate samples the corresponding contribution to the mobility varies as $T^{-1/2}$.

Behaviour at low temperature. Mobilities in the extrinsic range follow the rule observed in Ge, and tend to increase with time, as better samples are produced. $\mu_e=500\,000\text{ cm}^2/\text{voltsec}$ at 80°K seems to be the record

to date. It has been shown (Rollin and Petford 1955, Fritzsche and Lark-Horovitz 1955) that in the purest samples (which were not necessarily those with the highest Hall coefficient), mobilities increase down to liquid air temperature. In n-type samples Rollin and Petford found that R and σ were practically constant from 20° to 1.5°K , suggesting a vanishing small ionization energy of the donor centres. In p-type samples the acceptor ionization energy is 0.007 eV (Hrostowski *et al.* 1955), but, below about 16°K , R decreases sharply, a phenomenon observed in other semiconductors and one which has been attributed to conduction in an impurity band (Hung and Gliessman 1950, Hung 1950). The mobility in the acceptor band is of the order of $1\text{ cm}^2/\text{voltsec}$. The Hall mobility passes through a maximum at a somewhat higher temperature than that at which R is maximum. Essentially the same results have been obtained in p-type samples by Fritzsche and Lark-Horovitz. They found that the maximum of R shifts to higher T with increasing impurity concentration, as one may expect. At the same temperature a change of slope is found in the curves of $\ln \sigma$ versus $1/T$, and the transverse magnetoresistance effect, which at low temperatures is proportional to B and not to B^2 , becomes negative (at a temperature somewhat lower than that at which R reaches its maximum). It is evident that all these effects are connected, but their cause is still obscure. Conduction in an impurity band appears almost impossible with the small impurity concentrations of some of the specimens investigated, if the impurities are distributed uniformly. If they are distributed, say, along cracks or dislocations, Hung's hypothesis becomes more plausible and explains the behaviour of R and σ . (Incidentally, if this were a general feature of impurity centres, it would explain the rapid rate at which their activation energy decreases with their concentration.) The startling change of sign of the magnetoresistance effect is not however explained by conduction in an impurity band. No scattering mechanism will lead to an increase of conductivity on application of a magnetic field. Mackintosh (1956) has suggested an explanation assuming that the application of a magnetic field splits the donor levels into two sets separated by the Zeeman splitting. There is then a change in the number n of electrons in the conduction band, and, if the relative increase in n exceeds the relative decrease in the mobility, there may be a negative magnetoresistive effect. This theory needs refining before it may be compared with experiment; it indicates that the effect should be proportional to B^2 , whereas the observed dependence is linear. Another suggested explanation is a change of shape of the constant energy surfaces when a magnetic field is applied. Hatton and Rollin found another puzzling effect, namely the presence of a considerable longitudinal effect at the lowest temperatures. In the impurity band hypothesis, it would mean that the energy surfaces in this band are not spherical.

Another unexplained observation is the considerable magnetoresistance effect observed in degenerate samples (Mansfield 1955, Kanai 1955),

where, according to theory, the effect ought to be extremely small. It will be desirable to repeat on single crystals these observations carried out in polycrystalline materials. A longitudinal effect was also found, of the same order as the transverse effect. It appears likely that in the theory of the effects for which $\mu B > 1$ ($\omega\tau > 1$) quantization of the electron orbits in the magnetic field may play an essential role.

Band structure and effective masses. Isotropy of magnetoresistance (Pearson and Tanenbaum 1953, Hrostowski and Tanenbaum 1954) and of cyclotron resonances (Dresselhaus *et al.* 1955 a) indicates for the conduction band spherical energy surfaces at the centre of the elementary cell in momentum space. The latter experiment shows that, at liquid He temperatures, m_e^+ is a scalar and has the very low value $(0.013 \pm 0.001)m$. The line was clearly resolved at 2.2°K . There were indications of two types of holes with anisotropic masses of about $0.2m$ and $1.2m$. The variation of the Hall coefficient with B indicates a complicated valence band structure (Hrostowski *et al.* 1955). The electron spin resonance was also observed by Dresselhaus *et al.* (1955 a), with $g = 2.11 \pm 0.03$.

With the method of analysis of the optical absorption data suggested by Macfarlane and Roberts and described in § 3.2, Roberts and Quarrington (1955) found that the interband transition at the edge is indirect. The data do not fit a simple expression, as in Si and Ge, and point to a more complex band structure. There is evidence that the transition involves a phonon of an energy of 0.02 – 0.03 eV, which is not inconsistent with Herman's (1955) surmise that the holes may occupy the corners of the reduced zone. At these points, according to Herman, the band separation is large, and this is supported by the negligible change of the hole mobility with pressure. An attempt at interpretation of the optical data has been made by Blount *et al.* (1956). They are not inconsistent with the existence of two types of holes, as suggested by cyclotron resonances.

Further evidence on effective masses has been obtained from TEP measurements. Using the formula (in the intrinsic range)

$$Q = -\frac{k}{e} \left[\frac{b-1}{b+1} \left(\frac{E_G}{2kT} + 2 \right) + \frac{3}{4} \ln \frac{m_e^+}{m_h^+} \right].$$

Frederikse and Mielczarek (1955) found that $m_e^+/m_h^+ = 0.11$ at 300 – 400°K . In the impurity range they could fit their data with $m_e^+ = 0.014m$. Aigrain *et al.* (1956) obtained $m_e^+/m_h^+ = 0.13$ from thermo-magnetic experiments. Mansfield (private communication) could also fit TEP data on degenerate samples with $m_e^+ = 0.012m$. The hole mass cannot be similarly determined because p-type samples exhibit the phonon drag effect, which is not observed in n-samples since it varies with the power -3 of the carrier mean free path. A value $m_h^+ = 0.1m$ at high temperatures was obtained from TEP data by Tauc and Matyas (1955), who found also some evidence that this value increased at lower temperatures. Hrostowski *et al.* (1955) found that the electrical data at

low temperature could be fitted by taking effective masses of $0.015m$ for electrons and $0.17m$ for holes. Weiss (1956 a) obtained from TEP data at 333°K $m_e^+ = 0.037m$, $m_h^+ = 0.18m$, m_e^+ increasing at higher temperatures. Thus the heavy holes appear to be less abundant than the light ones.

Attempts to determine the hole effective mass have also been made by measuring, by the Faraday method, the diamagnetic susceptibility (Stevens and Crawford 1955), but were unsuccessful because the hole concentration was not large enough. The same experiment gave $m_e^+ = 0.028$ and $E_G(0^\circ\text{K}) = 0.26$.

Impurity levels. A theoretical study of substitutional impurity centres in InSb has been published by Rickayzen (1955) who has shown that it is justified to write the potential around an impurity in InSb as $e/\epsilon r$ ($\epsilon =$ dielectric constant), and that the trapped electron is practically unaffected by the polarization which it induces in the lattice. Hence for InSb the hydrogen-like model for impurity centres would be justified. With a dielectric constant of 17 (square of the infra-red refractive index), the ionization energy of the centres would then be

$$E_I = 13.5 m^+ / 289 = 0.047 m^+ \text{ ev},$$

where m^+ is the carrier effective mass, which for shallow centres has very nearly the same value as at the edge of the corresponding band. Hence for donors E_I would be $6 \times 10^{-4} \text{ ev}$, and for acceptors 0.0085 ev , using $m_h^+ = 0.18m$, and 0.056 using $m_h^+ = 1.2m$. The former value is not far from the experimental value 0.007 (Hrostowski *et al.* 1955).

Infra-red absorption. At high temperature the long wavelength absorption is the same for all samples and seems to be due to free carriers. However, absorption obeying the λ^2 law was observed only at and beyond about 100μ (Spitzer and Fan 1955). At low temperature, the absorption increases with λ for n-samples, but remains practically constant for p-samples (Avery *et al.* 1954, Kaiser and Fan 1955). Also, the absorption constant is not proportional to the density of free carriers. For both n- and p-samples, particularly in the latter, the absorption increases with decreasing T . The interpretation of these results is still obscure: electrical measurements prove that one cannot attribute the absorption to optical ionization of impurities, but it might be due to transitions between hydrogen-like levels of impurities. If that is so, the various lines should become separated on going to temperatures even lower than 5°K , the lowest temperature at which observations have been made so far. At longer waves, lattice bands were observed at 28 , 30 and 52μ , which Spitzer and Fan take to indicate some degree of ionic binding. The reflectivity has a sharp maximum at 56.4μ (Yoshinaga 1955, Yoshinaga and Oetjen 1956), presumably related to the absorption band at 52μ . The weak absorption at 28μ is apparently an overtone of the intense band at 56 . The reflectivity shows a temperature dependent

flat maximum beyond 100μ ; the minimum between this maximum and the peak at 56μ is strongly temperature dependent. All results at long waves are consistent with free carrier absorption.

Thermal conductivity. The thermal conductivity of InSb is very high, approaching that of a metal, and does not obey the T^{-1} law applying to the lattice contribution. However, this law is followed at low temperatures, and by extrapolation it is found that the behaviour of the extra term can be fitted by an expression $A \exp(-0.26/kT)$ (Busch and Schneider 1954), thus showing that it represents the electronic contribution, being proportional to the density of carriers. But the experimental values of this electronic contribution η_e are about 100 times larger than one would expect from the electrical conductivity according to the Wiedemann-Franz law. Fröhlich and Kittel (1954) have attempted to explain this effect taking into account the transport of ionization energy by the carriers created thermally at the hot end and recombining at the cold end. Writing qualitatively a Debye equation

$$\eta_e = C_e u \Lambda$$

(where C_e is the carrier heat capacity per unit volume, u their drift velocity and Λ their mean free path), and remembering that n is proportional to $\exp(-E_g/2kT)$, one finds that very roughly $C_e \sim nk(E_g/kT)^2$, instead of the normal expression nk , and the last factor may be as large as 100. This theory, however, assumes that the electron and hole mobilities are the same. But when one takes into account the fact that b is very large, one finds (Price 1955) that the ambipolar flow cannot account for the high value of η_e observed experimentally. As Price points out, the question of the origin of the high thermal conductivity may be settled by a combination of electrical and thermal measurements on the same crystal, particularly measurements of the Nernst effect in high fields. The anomalous Nernst effect due to ambipolar diffusion has been studied by Aigrain *et al.* (1956): the theory appears adequate and fits experimental data taking a ratio of effective masses $m_h^+/m_e^+ = 7.7$. According to Thuillier (1955) it is the transport of kinetic energy that is important in InSb, not that of ionization energy.

Photoconductivity and related effects. Lifetimes. InSb is a good photoconductor, photovoltaic junctions have been made, and the PEM effect is large. p-n junctions with rectification ratios if 10^4 have been grown using p-type melt and n-type seed (Mitchell *et al.* 1955), and also adding Zn to an n-type melt during crystal pulling (Kurnick *et al.* 1955). Their photosensitivity at low temperature is very high. On the surface near the junction, channel effects have been observed. In view of its small energy gap, InSb is thus a very important substance for infra-red studies and applications. But all photoeffects increase with decreasing temperature, when the cut-off moves to shorter waves; thus, sensitive InSb photocells would not have a spectral response extending beyond that of PbTe cells. It has been suggested that detectors based on the

PEM effect may be more sensitive than detectors based on ordinary photoconductivity.

A systematic investigation of lifetimes and of their variation with temperature has been carried out by Avery and Jenkins (1955) by the light spot method. It was found that the diffusion length was remarkably constant between 35 and 53μ for all p- and n-samples. In n-samples, τ too did not vary much between different specimens at room temperature ($2.4-3.5 \times 10^{-7}$ sec). For all n- and the purest p-type samples, τ increased with decreasing T from 350 to 200°K . At still lower temperatures τ dropped very sharply to below 10^{-8} , this being probably associated with the movement of the Fermi level. Also the response time of photovoltaic and photoconductive effects is of the order of a fraction of microsecond (Avery *et al.* 1954).

The combination of data from the PEM effect and the photoconductive response also gave values of τ between 5×10^{-8} and 5×10^{-7} , and the surface recombination velocity came out very large, about 10^6 cm/sec (Hilsum *et al.* 1955). Analysis of previous data, which ignored surface recombination, had led to much smaller values for τ . Kurnick and Zitter (1956) found that the dependence of the PEM response on B depends strongly on surface treatment, and they discuss on a simple theoretical model the best methods for determining from the observations the bulk lifetime, the mobilities, and possibly the surface recombination velocity. There has been no attempt to deduce diffusion lengths from the characteristics of p-n junctions.

It has been suggested that the bulk lifetime of added carriers in InSb is determined mainly by the rate of radiative recombination. The theory of this process, which has been given by van Roosbroeck and Shockley (1954), requires an accurate knowledge of the absorption spectrum near the edge. Avery and Jenkins (1955) did the calculation using the accurate absorption data at low level ($K < 250\text{ cm}^{-1}$) obtained by Roberts and Quarrington (1955) and estimating the absorption at high levels from the data given by Avery *et al.* (1954). The two ranges were joined by a plausible interpolation. This calculation gave a value of $1\mu\text{sec}$, with a possible error of a factor 5 in each direction. Mackintosh and Allen (1955) have based a similar calculation on the data of Avery *et al.* (1954) obtaining a value of $0.75\mu\text{sec}$, with an estimated error of a factor 2. More recently Goodwin and McLean (1956) have obtained a better knowledge of the absorption spectrum in the region $10^3 < K < 10^4\text{ cm}^{-1}$ from measurements of the PEM effect. They have recomputed the radiation lifetime using these data with the result $\tau = 0.36\mu\text{sec}$ in intrinsic material at room temperature, the estimated error being only 10%. Since lifetimes up to an appreciable fraction of a microsecond have been observed, it seems that, at room temperature, radiative recombination is in fact setting the limit on lifetimes. This appears to be confirmed by measurements by Moss and Hawkins (1956) of the intensity of the recombination radiation in very pure material.

This conclusion is of practical significance ; for it implies that the lifetime at room temperature will not be lengthened appreciably by further purification of the crystals or elimination of faults in the lattice. The hypothesis that τ is determined by radiative recombination is consistent with the observed dependence on the density of holes, and upon the temperature in the range 200 to 350°K.

It will be remembered that the radiative lifetime in Ge is 0.1 to 1 sec at room temperature. The lifetime in InSb is relatively short because the spectrum extends to much longer wavelengths, at which the density of the black body radiation is high, and because the absorption edge is very steep.

Nuclear magnetic resonance. Shulman *et al.* (1955) have observed nuclear magnetic resonances in InSb. They find that the observed widths of the lines cannot be explained in terms of the usual interactions, namely internuclear dipole-dipole interactions or interactions of the nuclear quadrupole moments with crystalline fields. They suggest that the broadening is due to nuclear spin exchange coupling through the hyperfine interaction of the nuclei with the carriers. Thus, in principle, measurements on the width can provide information on the band structure in the crystal, particularly in the normally inaccessible regions far from the Fermi level, and on the electronic wavefunctions.

Plasma resonance. A magnetoplasma resonance has been observed in InSb (Dresselhaus *et al.* 1955 b). Its position and shape agreed well with an elementary theory of the effect.

Applications. The applications of InSb as an infra-red detector have already been mentioned. The fact that the position of the edge may be varied in n-samples by changing the impurity content make it also suitable as an infra-red filter.

It was hoped that its high TEP might make it a good thermoelectric generator or refrigerator, but its thermal conductivity is too high (Goldsmid 1955).

Very interesting are the applications based on the high mobility, which causes high values of the Hall angle in relatively modest fields. The Hall effect is so large that an amplifier has been made, by using the input signal to magnetize a core in whose air gap is contained the crystal. An independent supply provides the current through the crystal and the signal collected at the Hall probes may show amplification. The ratio of the output power from the probes to the input power is given by

$$\frac{9\pi^2}{256} \frac{10^{-16}}{k} \mu^2 B^2,$$

where the numerical constant k depends on the geometry of the system, and generally has values between 2 and 5 (Saker *et al.* 1955). Amplification is only possible with the use of a high permittivity core and with a very thin crystal (Barlow 1955). There would be no limit to the amplification if B could increase without limit : in practice saturation occurs. The

device is limited to low frequencies and there are some difficulties, such as achieving thermal contact of the crystal with the core and matching the meter to the small impedance between the Hall probes. This type of apparatus may be used for the measurement of the intensities of magnetic fields, both low and high (though for high fields the magnetoresistive effect may be preferable), including the Earth's field (Ross and Saker 1955). A clip-on ammeter has also been made based on the same principle. Inserting a specimen of InSb in an electric line and making the current to generate also B , one has a power meter. Finally, InSb may be used with advantage in non-reciprocal four-terminal networks (resistance gyrator) instead of Ge, and as multiplier in analogue computers.

Table 1. Summary of properties of III-V compounds

Crystal structure : cubic, ZnS.

Space group : T_d^2

Comp.	Lattice par. A	Melt. point °C	Refr. index	Energy gap		Electron mob. 290°K cm ² /vsec	Hole mob. 290°K cm ² /vsec
				0°K ev	290°K ev		
Al P	5.42	~1050	3.4				
Al As	5.62	>1600		2.4(?)			
Al Sb	6.10	1060		1.60	1.52	50	150
Ga P	5.44			2.4	2.25		
Ga As	5.63	1280	3.4	1.5	1.35	4000	400
Ga Sb	6.09	725	3.9	0.78	0.70	5000	1000
In P	5.86	1050	3.3	1.4	1.3	3500	700
In As	6.06	942†	3.4	0.4	0.33	20000	
In Sb	6.48	523	4.1	0.23	0.17	80000	4000
In Bi	non-cubic			metallic			‡

† Under pressure.

‡ Bruns and Lautz (1954, 1955).

§ 5. THE I-V COMPOUNDS

These compounds are homologue either of KSb or of K₃Sb, the caesium compounds being the best studied. They are used in photocathodes and practically all research refers to the photoelectric effect. Thus the Li—Sb and K—Sb photocathodes have been investigated by Schaetti and Baumgartner (1953) (*q.v.* for previous references). The semi-conducting properties of the systems (K, Cs)Sb, In have been examined by Suhrmann and Kangro (1953) (*q.v.* for previous references). Thin layers exhibit, at certain compositions, a decrease of resistance with increasing temperature, from which the activation energies given in table 2 have been obtained. There is evidence that CsSb has a larger gap than Cs₃Sb because the wavelength of maximum photoelectric emission in Cs₃Sb photocathodes moves to shorter waves when Cs

evaporates off. The K—Sb compounds exhibit semiconducting properties over a range of compositions between KSb and K_3Sb , the energy gap apparently being smaller in the intermediate region. TEP indicated n-type conduction. Li_3Bi is also a semiconductor (Mooser and Pearson 1956 a) and it is the only known semiconducting compound of Bi.

A sample of In—Cs with 40% Cs also showed semiconducting properties, apparently with a small activation energy (0.2 ev): this actually would be a I—III compound, and would be remarkable since both elements are to the left of the Zintl boundary.

It is a pity so little is known on the properties of these semiconductors because at this stage a comparative study of the various groups of semiconductors in order to correlate their properties with their structure is very desirable. The only compound on which more systematic research has been carried out is Cs_3Sb (Boryak 1950, Boltaks and Zhuse 1952,

Table 2. Summary of properties of I—V compounds

Crystal structure : unknown

Compound	Melting point (°C)	Energy gap (ev)	Electron mobility $cm^2/vsec$
KSb	605	0.9	500
$CsSb$		0.8(?)	
Li_3Sb	>950		
K_3Sb	812	0.8	
Cs_3Sb		0.5–0.6	
Cs_3Bi		0.5–0.6	

Sakata 1953 a, b, c, d, 1954 a, b, Sakata and Munesue 1954, Miyazawa and Fukuhara 1952, Miyazawa 1953, Wallis 1956). Conductivity, Hall effect, optical absorption, TEP, magnetoresistance have been studied besides the external photoelectric effect. The energy gap is 0.5–0.6 ev and there are impurities activation energies of 0.2–0.3. From the energy distribution of the photoelectrons ejected by light of various wavelength, the top of the full band is estimated to be 1.9 ev below the vacuum level, and to sink, as T falls, at the rate of 3.5×10^{-4} ev/degree. From the thermoionic emission one gets a work function in fair agreement with the above result. It is remarkable that experiments of this kind have not been carried out for the better known S.I.C.

The layers are generally p-type, but can be made n-type by adding Cs. The acceptors are thus presumably vacant Cs sites and the substance behaves like an ionic crystal. Best purity achieved was 10^{16} . From magnetoresistance the electron mobility at room temperature is 500 and follows more or less the $T^{-3/2}$ law. Hole mobilities measured so far are much lower (~ 10).

§ 6. THE II-IV COMPOUNDS

6.1. General Considerations

Only results on the compounds of Mg and Ca have been published so far. The Mg compounds are cubic with the antiferite structure; the Ca compounds are tetragonal but do not deviate much from the antiferite structure. This structure has 12 atoms in the unit cell of volume a^3 : the atoms lie at the following positions, taking Mg_2Sn as typical:

$$\text{Sn } (0, 0, 0) \quad (0, \frac{1}{2}, \frac{1}{2}) \quad (\frac{1}{2}, 0, \frac{1}{2}) \quad (\frac{1}{2}, \frac{1}{2}, 0)$$

$$\text{Mg } \pm (\frac{1}{4}, \frac{1}{4}, \frac{1}{4}) \quad (\frac{1}{4}, \frac{3}{4}, \frac{3}{4})$$

$$(\frac{3}{4}, \frac{1}{4}, \frac{3}{4}) \quad (\frac{3}{4}, \frac{3}{4}, \frac{1}{4}).$$

The volume of the elementary cell in momentum space is $16/a^3$ and thus, since the atomic volume is $a^3/12$, there are $8/3$ states per atom in each band. As the three atoms together contribute 8 valence electrons, there are just as many states as electrons and these compounds are expected to be insulators or semiconductors (Mott and Jones 1936, p. 169).

Hume-Rothery and Raynor (1938) observed however that the fact that the stability of the II-IV compounds (and, for that matter, of all inter-metallic compounds) is greater the more electropositive the metal and the more electronegative the metalloid, together with the evidence of the crystal structure and of the regularities in melting point and heat of formation, supports the view that they are an extension of normal valency compounds into the region of weakly electronegative elements. In support of this view, they showed that Mg_2Sn forms little or no ternary solid solution with Al and In, even though an electron concentration of approximately $8/3$ is maintained. For a true electronic compound (i.e. a phase the structure of which is determined mainly by the ratio of electrons to atoms) such ternary solid solutions should exist. The conclusion is that Mg_2Sn and similar compounds may legitimately be regarded from different points of view.

Boltaks (1949) considers Mg_2Sn predominantly ionic. He observes that Mg and Sn are both paramagnetic. If the compound is a simple 'mixture' of the two, one would expect a paramagnetism, whereas, if it is ionic, it must be diamagnetic. Diamagnetism was in fact observed in stoichiometric samples, while a deviation of 3% from stoichiometry was sufficient to produce paramagnetism. Boltaks concluded that there is thus a proportion of ionic binding. However, diamagnetism must be expected in any pure semiconductor, that is to say a material in which configurations with unpaired spins are not thermally accessible at the temperature considered.

Welker on the other hand stresses the homopolar character of the bond, pointing out that the lattice of, say, Mg_2Si is very similar to that of Si. Every second atom of Si has been replaced by a pair of Mg atoms and there has been no change in the total number of valence electrons. In the compound two configurations are present, namely the configuration

$\text{Mg}_2^{2-}\text{Si}^{4+}$ in which each Mg atom forms a sp_3 -hybrid, and the configuration $\text{Mg}_2^{2+}\text{Si}^{4-}$ in which the complete octet on the Si atom is again represented by sp_3 orbitals. Hence presumably the ratio of the ionic to covalent contribution to the bond will remain small as in Si. If this is so, the II-IV compounds ought to have properties similar to those of the Group IV elements. There is in fact evidence that the II-IV compounds are nearer to the elements than the III-V.

6.2. Properties of the Various Compounds

Blunt *et al.* (1955): electrical and optical properties of Mg_2Sn .

Boltaks (1949 a, b): electrical properties and magnetic susceptibility of Mg_2Sn .

Brauer and Tiesler (1950): preparation; x-ray of Mg compounds.

Busch and Schneider (1954): thermal conductivity of Mg_2Sn .

Busch and Winkler (1953 a, 1954): preparation; R , σ versus T for Mg compounds.

Busch and Winkler (1953 b): mixed crystals of Mg_2Ge and Mg_2Sn .

Busch *et al.* (1954 c): preparation; x-ray; R , σ versus T for Ca compounds.

Lawson *et al.* (1955): electrical and optical properties, photoconduction of Mg_2Sn .

Long (1956): effect of pressure on the electrical properties of Mg_2Sn .

Robertson and Uhlig (1949): x-ray; σ versus T ; TEP; variation with composition for Mg—Sn, Mg—Pb.

Winkler (1955): R , σ versus T ; TEP of Mg compounds. Table of data on S.I.C.

The II-IV compounds are prepared by melting the elements together. The Mg compounds react with water vapour. In Mg_2Si and Mg_2Sn the reaction takes place only on a layer on the surface, but Mg_2Ge and Mg_2Pb break down completely into a powder. The Ca compounds are chemically unstable and, apart from the constants given in table 3, nothing is known about them. The most pure specimens of Mg_2Sn contained about 10^{16} extrinsic carriers cm^{-3} .

All energy gaps, except that for Mg_2Sn , have been derived only from electrical measurements. In general, values obtained from conductivity do not agree with those obtained from Hall effect, the latter being larger. This difference has been ascribed to failure of the mobilities to follow the $T^{-3/2}$ law, but it may also be due to the energy gap not varying linearly with temperature.

The best known of these compounds is Mg_2Sn . This substance demonstrates strikingly the difficulties of interpretation of optical absorption measurements: when one defines arbitrarily the edge at a constant, fairly high, level of absorption, one finds that it moves to longer wavelengths on heating, whereas, if the spectrum is analysed in the way suggested by Macfarlane and Roberts, the edge is found to move in the opposite direction.† This result is due to the fact that the edge is not steep

† The pressure dependence of the conductivity seems however to point to an increase of the energy gap on contraction (by about 0.01 eV between 1 and 2000 atmos).

and that its steepness varies with temperature. This is interpreted by supposing that the transitions at the edge are indirect, and that the phonon distribution varies in such a way that the edge becomes steeper as the temperature rises.

The analysis gives E_g as 0.12 eV at 0°K and 0.2 at room temperature.† However to obtain the latter value it is necessary to subtract from the absorption coefficient the contribution of a narrow band which appears at this temperature at a wavelength just beyond the band edge. This additional band may be due to intraband transitions of holes, of the type which occur in Ge. The small gap makes Mg_2Sn a suitable material for use in infra-red detectors, though it is not so easy to handle as the other possible materials, InSb and PbTe. A photoconductive response was observed at low temperature. At the lowest temperatures down to 4°K the Hall coefficient continues to increase indicating an impurity ionization energy of about 0.005 eV in samples of both types.

By comparing electrical data and the TEP, Winkler has obtained the following values for the combined effective mass: Mg_2Si , $m_c = (m_e + m_h)^{1/2} = 2m$; Mg_2Ge , $m_c = 2.8$; Mg_2Sn , $m_c = 0.4$. For Mg_2Sn the value obtained by combining electrical and optical data is $m_c = 0.5-0.6$. This value is rather larger than would be expected for a material with such a small energy gap. It may suggest that the interband gap is large both at the position in momentum space occupied by the electrons and at that occupied by the holes, or that one or both the band edges are degenerate. On the other hand the rather large mass values are consistent with the lower values of mobility than in the III-V compounds. There is some evidence that the combined mass increases with increasing T .

Analysis of the electrical data by the methods referred to in § 2.4 shows that the mobilities vary according to a $T^{-2.5}-T^{-3}$ law in all the magnesium compounds. In Mg_2Sn the mobility ratio remains at 1.2-1.3 at all temperatures. In this substance the highest mobilities observed were of the order of 1600 cm²/voltsec at 77°K.

Nothing is known about the band structure of these compounds except that in Mg_2Sn the two band edges do not occur at the same point in the Brillouin zone, for the optical absorption spectrum shows that the main interband transition is indirect. The energy of the phonon involved is about 0.015 eV (Pincherle, unpublished). This spectrum is qualitatively similar to that of Si and Ge.

The symmetry properties of the energy bands of the fluorite structure, and the lattice harmonics which are needed in cellular calculations of the band structure have been given by Bell (1954). If spin-orbit coupling is important, the bands will have to be characterized in terms of the irreducible representations of the direct product of the lattice group and a spinor group.

† Blunt *et al.* (1955) state that their results are difficult to reconcile with such a small energy gap.

There have been no experiments in which these materials were deliberately doped with, say, an element from Group V. Mixed crystals of Mg_2Ge and Mg_2Sn have been prepared. The lattice spacing varies almost linearly with composition, but the gap varies much more rapidly near 100% Mg_2Sn than elsewhere.

Table 3. Summary of properties of II–IV compounds

Crystal structure : Mg compounds, cubic, CaF_2 . Space group O_h^5 .
Ca compounds, tetragonal

Comp.	Lattice par. (Å)		Melt. point °C	Energy gap		Electron mob. 290°K cm^2/vsec	Hole mob. 290°K cm^2/vsec
	<i>a</i>	<i>c</i>		0°K ev	290°K ev		
Mg_2Si	6.34		1102		0.7–0.8	400	70
Mg_2Ge	6.38		1115		0.6–0.7	500	100
Mg_2Sn	6.76		778	0.12	0.20	300	250
Mg_2Pb	6.80		550	metallic			
Ca_2Si	9.43	10.19	920		1.9		
Ca_2Sn	12.15	11.93	1122		0.9		
Ca_2Pb			1110		0.4–0.5		

§ 7. THE II–V COMPOUNDS

The II–V compounds are homologue either of ZnAs_2 , or of ZnAs , or of Zn_3As_2 . No data on the first sub-group have been published recently, and there are only old reports that they may be used for cat-whisker detectors (e.g. Heike 1921). ZnP_2 and CdP_2 have a tetragonal structure, ZnAs_2 is orthorhombic.

Among the second sub-group, ZnSb and CdSb have attracted attention. Already in 1911 A. W. Smith was making conductivity, Hall effect, TEP, Nernst effect and magnetoresistance experiments on alloys of Sb with Bi, Cd and Zn and demonstrating the semiconducting properties of ZnSb and CdSb . When the nature of the unit cell had been established (the crystals are rhombic with 16 atoms in the unit cell), it became clear that, unless bands overlap, they would be semiconductors, since there are as many states as valence electrons (Justi and Lautz 1952 a, b, c). In this case it is impossible to envisage a stable saturated ionic bonding, and, with seven electrons, homopolar bonding is also to be excluded. ZnSb and CdSb should then be considered as true electronic compounds. Using the picture of the semiconducting bond (§ 1), each Sb atom is surrounded, approximately tetrahedrally, by two Cd (or Zn) and one Sb atom, and three covalent bonds are formed. The remaining two electrons presumably take the fourth tetrahedral position, so that each Sb atom forms sp_3 bonds and has a filled subshell; the number, *b*, of bonds between atoms of Group V is equal to one.

Pb is generally the most important impurity: it substitutes Sb and acts as an acceptor, hence most polycrystals are p-type. Ag and Ni instead act as donors, but they are probably located interstitially. An excess of one of the components also enters the lattice interstitially.

The energy gap of CdSb, from electrical measurements, is given as 0.52 by Justi and Lautz (1952 a, b) and as 0.48 by Busch and Winkler (1953 a). Several impurity activation energies were observed. Mobilities of 300–700 were obtained from magnetoresistance experiments, the effect being strictly quadratic. A peculiarity of this S.I.C. is that the hole mobility is larger than the electron mobility (Lautz 1953). CdSb has good rectifying properties.

Table 4. Summary of properties of II–V compounds

Comp.	Crystal Structure	Space Group	Lattice parameters (Å)			Melting point °C	Energy gap ev	Hole mob. cm ² /vsec
			<i>a</i>	<i>b</i>	<i>c</i>			
ZnSb	Orthorhombic		6.22	7.74	8.12	544	0.56	300
CdSb	Orthorhombic		6.47	8.25	8.53	453	0.48	300–700
Mg ₃ P ₂	Cubic	T _h ⁷	12.01					
Mg ₃ As ₂ †	Cubic	T _h ⁷	12.33			800		
Mg ₃ Sb ₂	Hexagonal	D _{3d} ³	4.57		7.23	930 (trans.)	0.8	100
Mg ₃ Bi ₂	Hexagonal	D _{3d} ³	4.67		7.40	715	metallic‡	
Zn ₃ P ₂	Tetragonal	D _{4h} ¹⁵	8.10		11.45	>420		
Zn ₃ As ₂ †	Tetragonal	D _{4h} ¹⁵	8.32		11.76	1015	0.9–1.1§	
Cd ₃ P ₂	Tetragonal	D _{4h} ¹⁵	8.75		12.28		0.5–0.6	
Cd ₃ As ₂	Tetragonal	D _{4h} ¹⁵	8.94		12.65		0.5	

† Natta and Passerini (1928 b).

‡ Grube *et al.* (1934).

§ 0.51 according to Harbeke and Lautz (1955).

The energy gap of ZnSb is given as about 0.7 by Devyatkov *et al.* (1952), as 0.6 by Mochan (1948) and as 0.56 by Busch *et al.* (1954). The hole mobility, again said to be higher than the electron mobility, was found to be low and did not vary much with temperature, but no good specimens have been investigated. ZnSb has a high TEP and may prove suitable for electrothermic refrigeration or thermoelectric power generation.

Data on some of the compounds of the third sub-group are given in table 4. Layers of Zn₃As₂ and Cd₃As₂ were found by Moss (1950 a) and by Braithwaite (1951) to be photoconductive, and from the long-wave cut-off E_G could be estimated. Zn₃P₂ has been studied by Lagrenaudie (1953, 1955), first on powders and then on small single crystals produced by distillation *in vacuo*. The energy gap is 1.1 ev from electrical and

photoconductivity measurements. The photoconductivity has a long time constant. The substance is not a good rectifier. Zn_3Sb_2 is also a semiconductor in some modifications (Bruns and Lautz 1954, 1955).

The best studied of these compounds is Mg_3Sb_2 . It has two phases, of which the hexagonal one has been examined. One would consider this substance as mainly ionic, but, as for Mg_2Sn , other points of view are possible. A discussion of the nature of the binding of binary Mg compounds was given by Zintl and Husemann (1933). A study of its zone structure was made by Kontorova (1948) using the nearly-free electron model developed by Jones (1934) to justify the Hume-Rothery rules. Although this method is inadequate at the zone boundary, the energy gap obtained, about 1 eV, was in agreement with experiment. The calculation predicted also some overlapping of the bands, so that at low temperature Mg_3Sb_2 should be a bad metal, but this has not been confirmed. The electric and thermoelectric properties were studied by Boltaks and Zhuse (1948), Zhuse *et al.* (1948), *q.v.* for earlier references, Busch *et al.* (1954 a, b); the photoconductivity by Zhuse *et al.* (1948) and by Moss (1950 b). These experiments agree in giving E_g as about 0.8 and showing that there are several impurity activation energies. The hole mobility at room temperature is of the order of 100, but no single crystals have been examined. Also in Mg_3Sb_2 $\mu_h > \mu_e$. The $T^{-3/2}$ law is obeyed at high temperatures. From TEP $m_c = (m_e + m_h)^{1/2} = 0.18 m$. The rectifying properties are good.

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The Elastic Constants of Anisotropic Materials—II.

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INTRODUCTION

IN 1946 the writer (Hearmon 1946) summarized work which had been published to the end of 1944 on the elastic constants of anisotropic materials, mainly crystals. The object of the present account is to bring this paper (referred to below as I) up to date by reviewing work published since that time. To avoid duplication of references, those given in I will not be repeated here, but will be cited in the form (I, 1) which indicates reference 1 in I. A few papers published before 1945 were either overlooked or not available when I was prepared, and these papers are included now.

During the period under review (roughly 1945–1955 inclusive), the books of Voigt (I, 115) and Wooster (I, 121) have been reprinted, and important new books published by Cady (1946) and Mason (1950 a). Mason's book includes a number of determinations of the elastic constants of crystals which have not been published elsewhere, and also summarizes results which had previously been published in various journals, mainly *Physical Review*. The papers containing these results are not in general included in the present bibliography, the reference usually being to Mason's book from which the original reference can be obtained if required.

A certain amount of work has appeared in Russian journals, but these journals have frequently proved to be unavailable, in spite of intensive search. In such cases, reliance has been placed on abstracts, particularly those in *Chemical Abstracts* and *Physical Abstracts*.

Since I was published, a few misprints and errors have become apparent, some of them only as a result of more recent work. The following corrections should be made to equations (I, 1.18)

$$\begin{aligned}s_{12}' &= (s_{11} + s_{22} - s_{66})m^2n^2 + s_{12}(m^4 + n^4) - (s_{16} - s_{26})mn(m^2 - n^2), \\ s_{36}' &= 2(s_{23} - s_{13})mn + s_{36}(m^2 - n^2), \\ s_{66}' &= 4(s_{11} + s_{22} - 2s_{12})m^2n^2 + 4(s_{26} - s_{16})mn(m^2 - n^2) + s_{66}(m^2 - n^2)^2,\end{aligned}$$

and equation (I, 7.5) should read

$$K = 3(s_{11} + 2s_{12}).$$

† Communicated by the Author

Modified values for the elastic constants of diamond and galena (originally given in refs. I, 8 and I, 9, and quoted in I) have been published (Bhagavantam and Bhimasenachar 1946, Bhagavantam and Seshagiri Rao 1951). Further work on β -brass (Artman and Thomson 1952, Lazarus 1949 b) indicates that Gcod's measurements of rigidity modulus (I, 47) are almost certainly in error. Figure 5 in I, although demonstrating qualitatively the effect of torsion-flexure coupling, is numerically inexact and the elastic constants of β -brass quoted in I are incorrect. The amended results for the three materials diamond, galena and β -brass are given below. (Table 7 A and B.)

§ 1. THEORY

1.1. *General Theory, Notation and Nomenclature*

A feature of the period under review has been the application of group theory (Bhagavantam and Suryanarayana 1949, Jahn 1949, Akulov and Feldshtein 1950, Rahman 1953, Gamba 1953) and tensor methods (Bechmann 1951 b, Fieschi and Fumi 1953, Fumi 1951, 1952 a, b, c, d, Hermann 1934, Jurmain 1948, Kaplan 1931, Laval 1951 b, le Corre 1953 c, Mason 1947, 1950 a, b, 1951, 1952, 1954, Niggli 1955, Schouten 1951, Wondratschek 1952, 1953) not only to elastic properties, but to the physical properties of crystals in general. The application of tensor methods to the theoretical study of the physical properties of crystals has also been discussed by Tournier (1947, 1953). Unfortunately, both of

Table 1. Notation for Stress and Strain Components

Stresses			Strains		
I.R.E.		I	I.R.E.		I
Tensor form	Matrix form	Matrix form	Tensor form	Matrix form	Matrix form
T_{11}	T_1	X_x	S_{11}	S_1	x_x
T_{22}	T_2	Y_y	S_{22}	S_2	y_y
T_{33}	T_3	Z_z	S_{33}	S_3	z_z
T_{23}	T_4	Y_z	$2 S_{23}$	S_4	y_z
T_{13}	T_5	Z_x	$2 S_{13}$	S_5	z_x
T_{12}	T_6	X_y	$2 S_{12}$	S_6	x_y

his papers contain a number of serious errors, and his results should therefore be used with caution. The main advantage of these methods is that they enable the theory to be presented more concisely, but their application has also led to the discovery (Bhagavantam 1942) of errors in the hitherto accepted schemes for the photoelastic constants of crystals (Pockels 1906, Bond, I, 15, Mason 1950 b), to the interpretation of electrostrictive and magnetostrictive effects (Mason 1947, 1950 a, 1951, 1954)

and to investigations of the 'third order' elastic coefficients (Birch 1947, Fumi 1951, 1952 b, Hearmon 1953).

In 1949 the Institution of Radio Engineers published its *Standards on Piezoelectric Crystals*, in which an agreed terminology and notation was formulated. This terminology differs in some respects from that used in I, and a comparison of the notations for stress and strain is given in table 1. The notation for the elastic constants s_{pq} and c_{pq} remains unaltered, but the names 'compliance' for the former and 'stiffness' for the latter are suggested.

Table 2. Equations for Rotated Elastic Constants

	C'_{11} (S'_{11})	C'_{12} (S'_{12})	C'_{14} $(\frac{S'_{14}}{2})$	C'_{15} $(\frac{S'_{15}}{2})$	C'_{16} $(\frac{S'_{16}}{2})$	C'_{66} $(\frac{S'_{66}}{4})$
$C_{11} (S_{11})$	α_1^4	$\alpha_1^2 \beta_1^2$	$\alpha_1^2 \beta_2 \gamma_1$	$\alpha_1^3 \gamma_1$	$\alpha_1^2 \beta_1 \gamma_1$	$\alpha_1^2 \beta_1^2$
$C_{22} (S_{22})$	$2\alpha_1^2 \alpha_2^2$	$\alpha_1^2 \beta_2^2 + \alpha_1^2 \beta_1^2$	$\alpha_1^2 \beta_2 \gamma_2 + \alpha_1^2 \beta_1 \gamma_1$	$\alpha_1 \alpha_2^3 \gamma_1 + \alpha_1^2 \alpha_2 \gamma_2$	$\alpha_1 \alpha_2 \beta_2 \gamma_1 + \alpha_1 \alpha_2 \beta_1 \gamma_2$	$2\alpha_1 \alpha_2 \beta_1 \beta_2$
$C_{33} (S_{33})$	$2\alpha_1^2 \alpha_2^2$	$\alpha_1^2 \beta_2^2 + \alpha_2^2 \beta_1^2$	$\alpha_1^2 \beta_2 \gamma_2 + \alpha_2^2 \beta_1 \gamma_1$	$\alpha_1 \alpha_2^2 \gamma_1 + \alpha_1^2 \alpha_2 \gamma_2$	$\alpha_1 \alpha_2 \beta_2 \gamma_1 + \alpha_1 \alpha_2 \beta_1 \gamma_2$	$2\alpha_1 \alpha_2 \beta_1 \beta_2$
$C_{14} (\frac{S_{14}}{2})$	$4\alpha_1^2 \alpha_2 \alpha_3$	$2\alpha_1^2 \beta_2 \beta_3 + 2\alpha_2 \alpha_3 \beta_1^2$	$\alpha_1^2 \beta_2 \gamma_2 + \alpha_2^2 \beta_2 \gamma_3 + 2\alpha_2 \alpha_3 \beta_1 \gamma_1$	$\alpha_1^2 \alpha_2 \gamma_1 + \alpha_2^2 \alpha_3 \gamma_2 + 2\alpha_2 \alpha_3 \alpha_1 \gamma_3$	$\alpha_1 \alpha_2 \beta_2 \gamma_1 + \alpha_1 \alpha_2 \beta_3 \gamma_2 + \alpha_2 \alpha_3 \beta_1 \gamma_1 + \alpha_1 \alpha_3 \beta_2 \gamma_3$	$2\alpha_1 \alpha_2 \beta_1 \beta_2 + 2\alpha_2 \alpha_3 \beta_1 \beta_3$
$C_{15} (\frac{S_{15}}{2})$	$4\alpha_1^2 \alpha_3$	$2\alpha_1^2 \beta_2 \beta_3 + 2\alpha_2 \alpha_3 \beta_1^2$	$\alpha_1^2 \beta_2 \gamma_2 + \alpha_2^2 \beta_3 \gamma_1 + 2\alpha_2 \alpha_3 \beta_1 \gamma_1$	$3\alpha_1^2 \alpha_3 \gamma_1 + \alpha_1^2 \gamma_3$	$\alpha_1^2 \beta_2 \gamma_1 + \alpha_1^2 \beta_2 \gamma_3 + 2\alpha_2 \alpha_3 \beta_1 \gamma_1$	$2\alpha_1^2 \beta_1 \beta_2 + 2\alpha_2 \alpha_3 \beta_1^2$
$C_{16} (\frac{S_{16}}{2})$	$4\alpha_1^2 \alpha_2$	$2\alpha_1^2 \beta_2 \beta_3 + 2\alpha_2 \alpha_3 \beta_1^2$	$\alpha_1^2 \beta_2 \gamma_2 + \alpha_2^2 \beta_3 \gamma_1 + 2\alpha_2 \alpha_3 \beta_1 \gamma_1$	$3\alpha_1^2 \alpha_2 \gamma_1 + \alpha_1^2 \gamma_2$	$\alpha_1^2 \beta_2 \gamma_2 + \alpha_1^2 \beta_2 \gamma_3 + 2\alpha_2 \alpha_3 \beta_1 \gamma_2$	$2\alpha_1^2 \beta_1 \beta_2 + 2\alpha_2 \alpha_3 \beta_1^2$
$C_{23} (S_{23})$	α_1^4	$\alpha_1^2 \beta_1^2$	$\alpha_1^2 \beta_2 \gamma_1$	$\alpha_1^3 \gamma_1$	$\alpha_1^2 \beta_2 \gamma_1$	$\alpha_1^2 \beta_1^2$
$C_{23} (S_{23})$	$2\alpha_1^2 \alpha_2^2$	$\alpha_1^2 \beta_2^2 + \alpha_2^2 \beta_1^2$	$\alpha_1^2 \beta_2 \gamma_2 + \alpha_2^2 \beta_1 \gamma_1$	$\alpha_1^2 \alpha_2 \gamma_2 + \alpha_2^2 \alpha_1 \gamma_1$	$\alpha_1 \alpha_2 \beta_2 \gamma_2 + \alpha_1 \alpha_2 \beta_1 \gamma_1$	$2\alpha_1 \alpha_2 \beta_1 \beta_2$
$C_{34} (\frac{S_{34}}{2})$	$4\alpha_1^2 \alpha_3$	$2\alpha_1^2 \beta_2 \beta_3 + 2\alpha_2 \alpha_3 \beta_1^2$	$\alpha_1^2 \beta_2 \gamma_2 + \alpha_2^2 \beta_3 \gamma_1 + 2\alpha_2 \alpha_3 \beta_1 \gamma_1$	$3\alpha_1^2 \alpha_3 \gamma_2 + \alpha_1^2 \gamma_3$	$\alpha_1^2 \beta_2 \gamma_2 + \alpha_1^2 \beta_2 \gamma_3 + 2\alpha_2 \alpha_3 \beta_1 \gamma_2$	$2\alpha_1^2 \beta_1 \beta_2 + 2\alpha_2 \alpha_3 \beta_1^2$
$C_{25} (\frac{S_{25}}{2})$	$4\alpha_1^2 \alpha_2 \alpha_3$	$2\alpha_1^2 \beta_2 \beta_3 + 2\alpha_2 \alpha_3 \beta_1^2$	$\alpha_1^2 \beta_2 \gamma_2 + \alpha_2^2 \beta_3 \gamma_1 + 2\alpha_2 \alpha_3 \beta_1 \gamma_1$	$\alpha_1^2 \alpha_2 \gamma_2 + \alpha_2^2 \alpha_3 \gamma_1 + 2\alpha_2 \alpha_3 \alpha_1 \gamma_3$	$\alpha_1 \alpha_2 \beta_2 \gamma_2 + \alpha_1 \alpha_2 \beta_3 \gamma_1 + \alpha_2 \alpha_3 \beta_2 \gamma_1 + \alpha_1 \alpha_3 \beta_2 \gamma_3$	$2\alpha_1 \alpha_2 \beta_1 \beta_2 + 2\alpha_2 \alpha_3 \beta_1 \beta_3$
$C_{26} (\frac{S_{26}}{2})$	$4\alpha_1^2 \alpha_2$	$2\alpha_1^2 \beta_2 \beta_3 + 2\alpha_2 \alpha_3 \beta_1^2$	$\alpha_1^2 \beta_2 \gamma_2 + \alpha_2^2 \beta_3 \gamma_1 + 2\alpha_2 \alpha_3 \beta_1 \gamma_1$	$3\alpha_1^2 \alpha_2 \gamma_1 + \alpha_1^2 \gamma_2$	$\alpha_1^2 \beta_2 \gamma_2 + \alpha_1^2 \beta_2 \gamma_3 + 2\alpha_2 \alpha_3 \beta_1 \gamma_2$	$2\alpha_1^2 \beta_1 \beta_2 + 2\alpha_2 \alpha_3 \beta_1^2$
$C_{33} (S_{33})$	α_1^4	$\alpha_1^2 \beta_1^2$	$\alpha_1^2 \beta_2 \gamma_1$	$\alpha_1^3 \gamma_1$	$\alpha_1^2 \beta_2 \gamma_1$	$\alpha_1^2 \beta_1^2$
$C_{34} (\frac{S_{34}}{2})$	$4\alpha_1^2 \alpha_3$	$2\alpha_1^2 \beta_2 \beta_3 + 2\alpha_2 \alpha_3 \beta_1^2$	$\alpha_1^2 \beta_2 \gamma_2 + \alpha_2^2 \beta_3 \gamma_1 + 2\alpha_2 \alpha_3 \beta_1 \gamma_1$	$3\alpha_1^2 \alpha_3 \gamma_2 + \alpha_1^2 \gamma_3$	$\alpha_1^2 \beta_2 \gamma_2 + \alpha_1^2 \beta_2 \gamma_3 + 2\alpha_2 \alpha_3 \beta_1 \gamma_2$	$2\alpha_1^2 \beta_1 \beta_2 + 2\alpha_2 \alpha_3 \beta_1^2$
$C_{35} (\frac{S_{35}}{2})$	$4\alpha_1^2 \alpha_3$	$2\alpha_1^2 \beta_2 \beta_3 + 2\alpha_2 \alpha_3 \beta_1^2$	$\alpha_1^2 \beta_2 \gamma_2 + \alpha_2^2 \beta_3 \gamma_1 + 2\alpha_2 \alpha_3 \beta_1 \gamma_1$	$3\alpha_1^2 \alpha_3 \gamma_1 + \alpha_1^2 \gamma_3$	$\alpha_1^2 \beta_2 \gamma_2 + \alpha_1^2 \beta_2 \gamma_3 + 2\alpha_2 \alpha_3 \beta_1 \gamma_2$	$2\alpha_1^2 \beta_1 \beta_2 + 2\alpha_2 \alpha_3 \beta_1^2$
$C_{36} (\frac{S_{36}}{2})$	$4\alpha_1^2 \alpha_2 \alpha_3$	$2\alpha_1^2 \beta_2 \beta_3 + 2\alpha_2 \alpha_3 \beta_1^2$	$\alpha_1^2 \beta_2 \gamma_2 + \alpha_2^2 \beta_3 \gamma_1 + 2\alpha_2 \alpha_3 \beta_1 \gamma_1$	$\alpha_1^2 \alpha_2 \gamma_2 + \alpha_2^2 \alpha_3 \gamma_1 + 2\alpha_2 \alpha_3 \alpha_1 \gamma_3$	$\alpha_1 \alpha_2 \beta_2 \gamma_2 + \alpha_1 \alpha_2 \beta_3 \gamma_1 + \alpha_2 \alpha_3 \beta_2 \gamma_1 + \alpha_1 \alpha_3 \beta_2 \gamma_3$	$2\alpha_1 \alpha_2 \beta_1 \beta_2 + 2\alpha_2 \alpha_3 \beta_1 \beta_3$
$C_{44} (\frac{S_{44}}{4})$	$4\alpha_1^2 \alpha_2^2$	$4\alpha_1 \alpha_2 \beta_1 \beta_2$	$2\alpha_1 \alpha_2 \beta_2 \gamma_1 + 2\alpha_2 \alpha_3 \beta_1 \gamma_2$	$2\alpha_1^2 \alpha_2 \gamma_2 + \alpha_2^2 \alpha_3 \gamma_1$	$\alpha_1^2 \beta_2 \gamma_2 + \alpha_1^2 \beta_2 \gamma_3 + \alpha_2 \alpha_3 \beta_1 \gamma_2$	$\alpha_1^2 \beta_2^2 + \alpha_2^2 \beta_1^2 + 2\alpha_1 \alpha_2 \beta_1 \beta_2$
$C_{45} (\frac{S_{45}}{4})$	$8\alpha_1 \alpha_2 \alpha_3^2$	$4\alpha_1 \alpha_2 \beta_1 \beta_3 + 4\alpha_2 \alpha_3 \beta_1 \beta_2$	$2\alpha_1 \alpha_2 \beta_2 \gamma_2 + 2\alpha_2 \alpha_3 \beta_1 \gamma_1 + 2\alpha_2 \alpha_3 \beta_2 \gamma_3 + 2\alpha_2 \alpha_3 \beta_1 \gamma_2$	$2\alpha_1^2 \alpha_3 \gamma_1 + 2\alpha_2 \alpha_3^2 \gamma_2 + 4\alpha_1 \alpha_2 \alpha_3 \gamma_3$	$\alpha_1^2 \beta_2 \gamma_2 + \alpha_1^2 \beta_2 \gamma_3 + \alpha_2 \alpha_3 \beta_2 \gamma_1 + \alpha_2 \alpha_3 \beta_2 \gamma_2 + 2\alpha_1 \alpha_2 \beta_1 \gamma_3$	$2\alpha_1 \alpha_2 \beta_1 \beta_2 + 2\alpha_2 \alpha_3 \beta_1 \beta_3 + 2\alpha_1 \alpha_2 \beta_2 \beta_3$
$C_{46} (\frac{S_{46}}{4})$	$8\alpha_1 \alpha_2 \alpha_3$	$4\alpha_1 \alpha_2 \beta_1 \beta_2 + 4\alpha_2 \alpha_3 \beta_1 \beta_2$	$2\alpha_1 \alpha_2 \beta_2 \gamma_2 + 2\alpha_2 \alpha_3 \beta_1 \gamma_1 + 2\alpha_2 \alpha_3 \beta_2 \gamma_3 + 2\alpha_2 \alpha_3 \beta_1 \gamma_2$	$2\alpha_1^2 \alpha_3 \gamma_1 + 2\alpha_2 \alpha_3^2 \gamma_2 + 4\alpha_1 \alpha_2 \alpha_3 \gamma_3$	$\alpha_1^2 \beta_2 \gamma_2 + \alpha_1^2 \beta_2 \gamma_3 + \alpha_2 \alpha_3 \beta_2 \gamma_1 + \alpha_2 \alpha_3 \beta_2 \gamma_2 + 2\alpha_1 \alpha_2 \beta_1 \gamma_3$	$2\alpha_1 \alpha_2 \beta_1 \beta_2 + 2\alpha_2 \alpha_3 \beta_1 \beta_3 + 2\alpha_1 \alpha_2 \beta_2 \beta_3$
$C_{55} (\frac{S_{55}}{4})$	$4\alpha_1^2 \alpha_2^2$	$4\alpha_1 \alpha_2 \beta_1 \beta_2$	$2\alpha_1 \alpha_2 \beta_2 \gamma_1 + 2\alpha_2 \alpha_3 \beta_1 \gamma_2$	$2\alpha_1^2 \alpha_2 \gamma_2 + 2\alpha_2^2 \alpha_3 \gamma_1$	$\alpha_1^2 \beta_2 \gamma_2 + \alpha_1^2 \beta_2 \gamma_3 + \alpha_2 \alpha_3 \beta_1 \gamma_2$	$\alpha_1^2 \beta_2^2 + \alpha_2^2 \beta_1^2 + 2\alpha_1 \alpha_2 \beta_1 \beta_2$
$C_{56} (\frac{S_{56}}{4})$	$8\alpha_1^2 \alpha_2 \alpha_3$	$4\alpha_1 \alpha_2 \beta_1 \beta_2 + 4\alpha_2 \alpha_3 \beta_1 \beta_2$	$2\alpha_1 \alpha_2 \beta_2 \gamma_2 + 2\alpha_2 \alpha_3 \beta_1 \gamma_1 + 2\alpha_2 \alpha_3 \beta_2 \gamma_3 + 2\alpha_2 \alpha_3 \beta_1 \gamma_2$	$2\alpha_1^2 \alpha_3 \gamma_1 + 2\alpha_2^2 \alpha_3 \gamma_2 + 4\alpha_1 \alpha_2 \alpha_3 \gamma_3$	$\alpha_1^2 \beta_2 \gamma_2 + \alpha_1^2 \beta_2 \gamma_3 + \alpha_2 \alpha_3 \beta_2 \gamma_1 + \alpha_2 \alpha_3 \beta_2 \gamma_2 + 2\alpha_1 \alpha_2 \beta_1 \gamma_3$	$2\alpha_1^2 \beta_1 \beta_2 + 2\alpha_2 \alpha_3 \beta_1 \beta_3 + 2\alpha_1 \alpha_2 \beta_2 \beta_3$
$C_{66} (\frac{S_{66}}{4})$	$4\alpha_1^2 \alpha_2^2$	$4\alpha_1 \alpha_2 \beta_1 \beta_2$	$2\alpha_1 \alpha_2 \beta_2 \gamma_2 + 2\alpha_2 \alpha_3 \beta_1 \gamma_1$	$2\alpha_1^2 \alpha_2 \gamma_1 + 2\alpha_2^2 \alpha_3 \gamma_2$	$\alpha_1^2 \beta_2 \gamma_2 + \alpha_1^2 \beta_2 \gamma_3 + \alpha_2 \alpha_3 \beta_2 \gamma_1 + \alpha_2 \alpha_3 \beta_2 \gamma_2$	$\alpha_1^2 \beta_2^2 + \alpha_2^2 \beta_1^2 + 2\alpha_1 \alpha_2 \beta_1 \beta_2$

In tensor notation, the generalized Hooke's law is

$$\text{or} \quad \left. \begin{array}{l} S_{ij} = s_{ijkl} T_{kl} \\ T_{ij} = c_{ijkl} S_{kl} \end{array} \right\} i, j, k, l = 1, 2 \text{ or } 3, \quad \left. \begin{array}{l} T_{ij} = T_{ji}, \\ S_{ij} = S_{ji}, \end{array} \right\} \quad \dots \quad (1.11)$$

and in matrix notation

$$\text{or} \quad \left. \begin{array}{l} S_p = s_{pq} T_q \\ T_p = c_{pq} S_q \end{array} \right\} p, q = 1, 2, 3, 4, 5 \text{ or } 6 \quad \dots \quad (1.12)$$

in which the usual convention is adopted whereby repetition of a suffix implies summation with respect to that suffix. The stiffnesses c_{pq} can be derived from the c_{ijkl} simply by writing the suffixes

$$1 \text{ for } 11, 2 \text{ for } 22, 3 \text{ for } 33, 4 \text{ for } 23, 5 \text{ for } 13, 6 \text{ for } 12. \quad \dots \quad (1.13)$$

Thus, for example $c_{1123} = c_{1132} = c_{3211} = c_{2311} = c_{14}$. Owing to the occurrence of the factor 2 in the definition of the tensor shear strain components, the direct change over cannot be made for the compliances. Instead, the suffixes are contracted according to the scheme (1.13), and the following rules applied:

$$\left. \begin{array}{l} \text{If } p=1, 2 \text{ or } 3, \quad q=1, 2 \text{ or } 3, \quad s_{iijj} = s_{pq}, \\ \text{If } p=1, 2 \text{ or } 3, \quad q=4, 5 \text{ or } 6, \quad s_{iijk} = s_{pq}/2, \\ \text{If } p=4, 5 \text{ or } 6, \quad q=4, 5 \text{ or } 6, \quad s_{ijkl} = s_{pq}/4. \end{array} \right\} \quad \dots \quad (1.14)$$

Under a change of co-ordinate axes specified by

$$\left. \begin{array}{l} x' = \alpha_1 x + \alpha_2 y + \alpha_3 z, \\ y' = \beta_1 x + \beta_2 y + \beta_3 z, \\ z' = \gamma_1 x + \gamma_2 y + \gamma_3 z, \end{array} \right\} \quad \dots \quad (1.15)$$

the compliances are transformed according to the equation

$$s'_{ijkl} = i_m j_n k_o l_p s_{mnop}, \quad \dots \quad (1.16)$$

where i, j, k, l on the right hand side now represent α, β and γ , writing 1 for α , 2 for β and 3 for γ . Similarly

$$c'_{ijkl} = i_m j_n k_o l_p c_{mnop}. \quad \dots \quad (1.17)$$

Application of eqns. (1.16) and (1.17) together with the conditions (1.14) enables table 2 to be constructed (Hearmon 1947, see also Bechmann 1951 b). This table gives the explicit equations for the transformation of typical elastic constants under the rotation (1.15). It is to be read downwards, so that, for example

$$\begin{aligned} c_{11}' &= \alpha_1^4 c_{11} + \dots + 4\alpha_1^2 \alpha_2 \alpha_3 c_{14} + \dots + 4\alpha_1^2 \alpha_2^2 c_{66}, \\ s_{11}' &= \alpha_1^4 s_{11} + \dots + 4\alpha_1^2 \alpha_2 \alpha_3 s_{14}/2 + \dots + 4\alpha_1^2 \alpha_2^2 s_{66}/4, \\ c_{14}' &= \alpha_1^2 \beta_1 \gamma_1 c_{11} + \dots + (\alpha_1^2 \beta_3 \gamma_2 + \alpha_1^2 \beta_2 \gamma_3 + 2\alpha_2 \alpha_3 \beta_1 \gamma_1) c_{14} + \dots \\ &\quad + (2\alpha_1 \alpha_2 \beta_1 \gamma_2 + 2\alpha_1 \alpha_2 \beta_2 \gamma_1) c_{66}, \\ s_{14}'/2 &= \alpha_1^2 \beta_1 \gamma_1 s_{11} + \dots + (\alpha_1^2 \beta_3 \gamma_2 + \alpha_1^2 \beta_2 \gamma_3 + 2\alpha_2 \alpha_3 \beta_1 \gamma_1) s_{14}/2 + \dots \\ &\quad + (2\alpha_1 \alpha_2 \beta_1 \gamma_2 + 2\alpha_1 \alpha_2 \beta_2 \gamma_1) s_{66}/4. \end{aligned}$$

Table 2 therefore gives the equations for deriving the compliances and stiffnesses with suffixes 11, 12, 14, 15, 56 and 66 of a triclinic crystal in the

directions specified by eqns. (1.15). The equations for the remaining constants can be derived from those in table 2 by suitable interchange of α , β and γ as given in table 3.

As stated in the editorial footnote to table 1 of I, the convention in crystallography is to identify the two-fold axis of monoclinic crystals with the y axis, but Voigt (I, 115) identified the two-fold axis with z . The

Table 3. Rotated Elastic Constants

To derive	$c'_{22} (s'_{22})$	substitute β for α in the equation for	$c'_{11} (s'_{11})$
" "	$c'_{33} (s'_{33})$	" γ " α " "	$c'_{11} (s'_{11})$
" "	$c'_{13} (s'_{13})$	" γ " β " "	$c'_{12} (s'_{12})$
" "	$c'_{23} (s'_{23})$	" γ " α " "	$c'_{12} (s'_{12})$
" "	$c'_{25} (s'_{25}/2)$	" $\left\{ \begin{matrix} \alpha & \beta \\ \beta & \alpha \end{matrix} \right\}$ " "	$c'_{14} (s'_{14}/2)$
" "	$c'_{36} (s'_{36}/2)$	" $\left\{ \begin{matrix} \alpha & \gamma \\ \gamma & \alpha \end{matrix} \right\}$ " "	$c'_{14} (s'_{14}/2)$
" "	$c'_{16} (s'_{16}/2)$	" β " γ " "	$c'_{15} (s'_{15}/2)$
" "	$c'_{24} (s'_{24}/2)$	" β " α " "	$c'_{15} (s'_{15}/2)$
" "	$c'_{26} (s'_{26}/2)$	" $\left\{ \begin{matrix} \beta & \alpha \\ \alpha & \gamma \end{matrix} \right\}$ " "	$c'_{15} (s'_{15}/2)$
" "	$c'_{34} (s'_{34}/2)$	" $\left\{ \begin{matrix} \beta & \gamma \\ \gamma & \alpha \end{matrix} \right\}$ " "	$c'_{15} (s'_{15}/2)$
" "	$c'_{35} (s'_{35}/2)$	" $\left\{ \begin{matrix} \alpha & \gamma \\ \gamma & \alpha \end{matrix} \right\}$ " "	$c'_{15} (s'_{15}/2)$
" "	$c'_{45} (s'_{45}/4)$	" $\left\{ \begin{matrix} \alpha & \gamma \\ \gamma & \alpha \end{matrix} \right\}$ " "	$c'_{56} (s'_{56}/4)$
" "	$c'_{46} (s'_{46}/4)$	" $\left\{ \begin{matrix} \alpha & \beta \\ \beta & \alpha \end{matrix} \right\}$ " "	$c'_{56} (s'_{56}/4)$
" "	$c'_{44} (s'_{44}/4)$	" γ " α " "	$c'_{66} (s'_{66}/4)$
" "	$c'_{55} (s'_{55}/4)$	" γ " β " "	$c'_{66} (s'_{66}/4)$

question of the best choice of axes in the monoclinic system remained an academic one until measurements were actually made by Mason in 1946 of all the elastic constants of the monoclinic crystal, di-potassium tartrate (DKT). Since then, other complete measurements on monoclinic crystals have been made by Mason himself (1950 a), Bechmann (1950, 1952 b), Sundara Rao (1949 d) and Bechmann and Ayers (1954). In reporting the results of their measurements, Mason and Bechmann have followed the crystallographic convention (y axis 2-fold), but in the cases of lithium sulphate monohydrate and DKT, Bechmann (1952 b) and Bechmann and Ayers (1954) have chosen orientations for the x and z axes differing from those chosen by Mason (1950 a). Furthermore, Sundara Rao (1949 d), whose results were the second to be reported on a

monoclinic material, followed Voigt's convention (z axis two-fold). In the same month as Sundara Rao's paper appeared, the Institution of Radio Engineers (1949) published their *Standards on Piezoelectric Crystals* and recommended the adoption of the crystallographic convention in preference to that of Voigt. It is therefore now advisable to adhere to the I.R.E. convention, but until it is universally adopted, the possibility of confusion obviously exists.

1.2. Third Order Elastic Constants

The generalized Hooke's law implies a linear relation between the components of stress and strain, and in its matrix form is given by (1.12). In practice, most, if not all, materials show some departure from linearity. Formally, this means that the stress components will be given by polynomial functions of the strain components, and not by linear functions. The use of full polynomial functions is ruled out on grounds of complexity, but a better approximation than (1.12) is obtained if quadratic terms in the strains are included so that (1.12) becomes

$$T_m = c_{mn} S_n + c_{mqr} S_q S_r,$$

and the elastic stiffnesses c_{pq} are no longer independent of stress. This dependence on stress provides an instructive example of the use of tensor methods in crystal physics, and although the practical use of the analysis is probably limited to systems under hydrostatic stress, it will be considered here in some detail.

The most convenient formulation of the problem is in terms of the strain energy function. Provided the strains (S) are sufficiently small, the elastic energy stored in a deformed anisotropic material can be written in tensor notation :

$$\phi = \frac{1}{2} c_{ijkl} S_{ij} S_{kl} \quad \dots \quad (1.21)$$

If the strains are not small, then a closer approximation is obtained by including terms of higher degree in the strains than the second. Thus, including third degree products

$$\phi = \frac{1}{2} c_{ijkl} S_{ij} S_{kl} + c_{ijklmn} S_{ij} S_{kl} S_{mn} \quad \dots \quad (1.22)$$

The c_{ijklmn} are components of a sixth rank tensor containing 729 components, of which 56 are independent for a triclinic material (Kaplan 1931). Birch (1947) writes the contribution of the third order terms to the strain energy in the form :

$$\phi_3 = \Sigma C_{pqr} \eta_p \eta_q \eta_r \quad \dots \quad (1.23)$$

where p, q, r may take any values from 1 to 6, subject to the condition $p \leq q \leq r$, and the summation convention is not implied. The relations between the η_x and S_{ij} are simply :

$$\eta_1 = S_{11}, \eta_2 = S_{22}, \eta_3 = S_{33}, \eta_4 = S_{23}, \eta_5 = S_{13}, \eta_6 = S_{12} \quad \dots \quad (1.24)$$

Birch showed for those cubic classes characterised by two-fold cubic axes, the independent 'third order' coefficients C_{pqr} are :

$$C_{111}, C_{112}, C_{113}, C_{144}, C_{155}, C_{166}, C_{123} \text{ and } C_{456},$$

whereas for the remaining cubic classes (those characterized by four-fold cubic axes) there are two additional relations

$$C_{113}=C_{112}, C_{155}=C_{166},$$

which reduce the number of independent coefficients from 8 to 6.

Table 4. Crystal Classes, and Numbers of Independent Coefficients

System	Crystal classes Hermann-Mauguin symbols	Numbers of coefficients		
		Elastic		Photo- elastic
		2nd order	3rd order	
Triclinic	1, $\bar{1}$	21	56	36
Monoclinic	2, m , $\frac{2}{m}$	13	32	20
Orthorhombic	$2mm$, 222 , $\frac{2}{m} \frac{2}{m} \frac{2}{m}$	9	20	12
Tetragonal	a 4, $\bar{4}$, $\frac{4}{m}$	7	16	10
	b $4mm$, $\bar{4}2m$, 422 , $\frac{4}{m} \frac{2}{m} \frac{2}{m}$	6	12	7
Trigonal	a 3, $\bar{3}$	7	20	12
	b $3m$, $\bar{3} \frac{2}{m}$, 32	6	14	8
Hexagonal	a 6, $\bar{6}$, $\frac{6}{m}$	} 5	12	8
	b $6mm$, $\bar{6}m2$, 622 , $\frac{6}{m} \frac{2}{m} \frac{2}{m}$		10	6
Cubic	a 23 , $\frac{2}{m} \bar{3}$	} 3	8	4
	b $\bar{4}3m$, 432 , $\frac{4}{m} \bar{3} \frac{2}{m}$		6	3

Actually, Birch classified one of the cubic classes wrongly, and the error was pointed out shortly afterwards by Bhagavantam and Suryanarayana (1947 b, 1949). These workers applied Bhagavantam's group theoretical method (1942) to the evaluation of the number of independent third order elastic constants in each of the 32 crystal classes. Their results, which have been confirmed by Jahn (1949), are given in table 4 together with the

numbers of photoelastic coefficients (Bhagavantam 1942) and of the usual second order elastic constants.

The second column of table 4 contains the Hermann–Mauguin symbols for the crystal classes (Phillips 1946). This notation possesses considerable advantages over that of Schönflies, since it enables the characteristic symmetry elements in each class to be seen at a glance.

There are two sub-groups in each of the last four systems in table 4, the criterion for the sub-division being the presence or absence of a two-fold axis, or its equivalent, normal to the principal axis, except in the cubic system, for which the criterion is the presence of two or four-fold cubic axes. In the cubic and hexagonal systems there is, however, no sub-division as far as second order elastic coefficients are concerned.

More recently Fumi (1951, 1952 b) and Hearmon (1953) have given not only the numbers, but also the actual schemes of third-order coefficients in all crystal classes. Extension of the results to isotropic materials (Murnaghan 1951, Krishna Murty 1952, Hearmon 1953) shows that the scheme of coefficients for these materials contains three independent coefficients, as predicted earlier by Jahn (1949).

The concept of third order elastic constants has found application in the interpretation of the effect of pressure on the second order elastic constants of cubic crystals (Birch 1947, Lazarus 1949 a, Hearmon 1953, see § 2.4). Mention should also be made of the work of Mason, who has also considered problems involving tensors of high rank in the interpretation of the electrostriction of Rochelle salt (1950 a), the magnetostriction of nickel (1951), and cobalt (1954), and the antiferroelectric behaviour of deuterated ammonium di-hydrogen phosphate (1952).

1.3. *The Atomic and Lattice Theory of the Elastic Constants*

In this section, the aim is limited to indicating the various approaches which have been made to the theoretical calculation of the elastic constants and to comparing, as far as possible, the calculated and observed values. For an account of the theory, reference should be made to text-books (e.g. Mott and Jones 1936, Seitz I, 103, Boas 1947, Kittel 1953, Born and Huang 1954) and to original papers (e.g. Fuchs I, 35, 36, Kellerman 1940, Fuchs and Peng I, 37, Begbie and Born 1946, Begbie 1946, Löwdin 1948, Jones 1949, Huang 1950, Leibfried 1951, Mott 1952, Wooster 1953).

It is possible to distinguish broadly two interrelated approaches. In the first, typified by the papers of Fuchs (I, 35, 36), Bulashevich (1941), Salnikov (1945), Löwdin (1948), and others, the aim is to calculate the elastic constants from purely theoretical considerations. The classical theory of Born (Born and Göppert-Meyer 1933) regards ionic crystals as made up of positive and negative ions, the attraction between the oppositely charged ions being balanced by repulsive forces which vary more rapidly with distance than do the Coulomb forces. The repulsive forces

can only be accounted for fully in terms of wave mechanics. Later refinements to the original treatment have allowed the contributions of other interactions to be assessed and have also extended the treatment to metallic crystals. The calculation by quantum mechanical methods of all the terms contributing to the elastic constants is an extremely formidable problem, and involves heavy numerical work, even when approximate methods are used (Löwdin 1948).

Table 5 summarizes some recent calculations of the values of elastic constants at absolute zero by various methods and compares the results with experimental values at room temperature; for details, reference should be made to the original papers. Other calculations on alkali halide crystals have been made by Tolpygo (1950) and Brauer (1951), and on diamond structures by Wohlfarth (1952). It will be noted that all the materials in table 5 belong to the cubic system and, with the exception of sodium and copper, are alkali halides. The observed values are the average of those at present available, and bracketed values were obtained by difference.

The agreement is reasonably close, but it has to be remembered that there are no experimental results at 0°K with which to compare the calculations. In general, the stiffnesses increase with decreasing temperature, so that in some cases, the discrepancies already present in the above table would be increased if a true comparison at 0°K were possible.

In the classical work of Born (Born and Göppert-Meyer 1933) some of the difficulties of the treatment were avoided by taking empirical data, for instance, the interionic distance and the compressibility as a basis for the calculations. The elastic constants are the derivatives of the potential energy with respect to stress or strain, summed over the lattice, and the potential energy can be obtained in terms of the force field. Thus if the force field is known, the elastic constants can be calculated. These ideas lie behind the second, but related method of approach to the calculation of the elastic constants. One of the first to use this method was Nagendra Nath (1935) who, in his work on diamond, derived expressions for the elastic constants in terms of the force constants between the atoms in the lattice; other workers (Dayal 1944, Bhagavantam 1946, Krishnamurti 1951, Kobayashi 1952) have more recently discussed the further application of the method to the calculation of the elastic constants of diamond. By introducing certain approximations (Dayal 1944), the expressions obtained by Nath for these constants become

$$\left. \begin{aligned} c_{11} &= (K_1 + 12K_\alpha + 12K_\beta)/3d, \\ c_{12} &= (K_1 - 6K_\alpha + 6K_\beta)/3d, \\ c_{44} &= 2(3K_\alpha + K_\beta)/d, \end{aligned} \right\} \quad . \quad . \quad . \quad (1.31)$$

where K_1 is the force constant referring to nearest neighbour atom pairs, K_α is the force constant for angular displacement of the valence bonds meeting at an atom, K_β is the force constant referring to next nearest neighbours, d is the length of side of the unit cube.

Table 5. Observed and Calculated Elastic Stiffnesses
Unit= 10^{11} dynes/cm²

Material	Calc (C) or Obs (O)	c_{11}	c_{12}	c_{44}	$c_{11} - c_{12}$	Reference
Cu	C	—	—	9.8	6.2	(1)
	C	—	—	8.6	4.9	(7)
Na	O	17.1	12.2	6.9	(4.9)	(1)
	C	—	—	0.67	0.25	(1)
Cs Br	O	0.52	0.40	0.41	(0.12)	(3)
Cs Br	C	3.5	0.6	0.6	(2.9)	(3)
Cs Cl	C	4.0	0.6	0.6	(3.4)	(3)
Cs F	C	5.1	1.0	1.0	(4.1)	(3)
Cs I	C	2.8	0.6	0.6	(2.2)	(3)
KBr	C	—	—	0.77	2.59	(6)
	C	3.5	0.7	0.7	(2.8)	(3)
KBr	O	3.51	0.575	0.569	(2.94)	(3)
	C	—	—	0.92	2.62	(6)
KCl	C	3.8	0.60	0.95	(3.2)	(4)
	C	3.9	0.8	0.8	(3.1)	(3)
KCl	O	3.97	0.613	0.685	(3.36)	(3)
	C	—	1.49	1.76	—	(4)
KF	C	6.1	1.6	1.6	(4.5)	(3)
	C	—	—	0.61	2.19	(6)
KI	C	3.1	0.5	0.5	(2.6)	(3)
	O	2.68	0.43	0.39	(2.25)	(3)
Li Br	C	4.8	1.4	1.4	(3.4)	(3)
Li Cl	C	—	1.5	2.01	—	(4)
	C	5.5	1.8	1.8	(3.7)	(3)
Li F	C	—	3.76	5.70	—	(4)
	C	10.7	4.9	4.9	(5.8)	(3)
Li I	O	11.0	4.5	5.6	(6.5)	(3)
	C	4.2	1.0	1.0	(3.2)	(3)
Na Br	C	4.3	1.0	1.0	(3.3)	(3)
	O	3.58	1.14	1.15	(2.44)	(3)
Na Br	C	4.65	1.28	1.28	(3.37)	(2)
	C	—	—	1.81	2.04	(6)
Na Cl	C	4.5	0.98	1.53	(3.5)	(4)
	C	—	1.03	1.51	—	(5)
Na Cl	C	5.0	1.3	1.3	(3.7)	(3)
	O	4.86	1.25	1.26	(3.61)	(3)
Na F	C	3.4	2.34	3.28	(1.06)	(4)
	C	8.5	2.8	2.8	(5.7)	(3)
Na I	C	3.8	0.7	0.7	(3.1)	(3)
RbBr	C	3.2	0.6	0.6	(2.6)	(3)
RbCl	C	3.6	0.7	0.7	(2.9)	(3)
RbF	C	5.4	1.3	1.3	(4.1)	(3)
Rb I	C	2.8	0.4	0.4	(2.4)	(3)

(1) Bulashevich (1941), (2) Kellerman (1940), (3) Krishnan and Roy (1952),
(4) Löwdin (1948), (5) Lundqvist (1952), (6) Price (1947), (7) Salnikov
(1945).

Dayal (1944) has used the observed features of the fluorescence, absorption and Raman spectra of diamond to evaluate the force constants as

$K_1=3.14 \times 10^5$; $K_\alpha=0.197 \times 10^5$; $K_3=0.39 \times 10^5$ dynes/cm, which when inserted into eqns. (1.31) together with $d=3.552 \times 10^{-8}$ cm give

$$c_{11}=96 \times 10^{11}; \quad c_{12}=40 \times 10^{11}; \quad c_{44}=56 \times 10^{11} \text{ dynes/cm}^2.$$

The experimental values of Bhagavantam and Bhimasenachar (1946) are

$$c_{11}=95 \times 10^{11}; \quad c_{12}=39 \times 10^{11}; \quad c_{44}=43 \times 10^{11} \text{ dynes/cm}^2.$$

The agreement is close for c_{11} and c_{12} ; Bhagavantam (1946) has applied Born's method and obtained a revised equation for c_{44} which leads to a value of 44×10^{11} dynes/cm², in better agreement with experiment.

The most recent theoretical estimate (Krishnamurti 1951) is $c_{44}=42 \times 10^{11}$, but Krishnamurti himself implies that there is some uncertainty associated with this estimate. There has also been some controversy (Born 1946, Smith 1948, Krishnan 1948) regarding the basic lattice dynamics and the interpretation of the Raman frequencies, all of which confirms that the final solution of the problem of calculating elastic constants has by no means been reached.

Other materials on which calculations have been carried out are aluminium (Leigh 1951 *a*), β -brass (Jones 1952 *a*), barium titanate (Devonshire 1951), quartz (Saksena 1944), ice (Penny 1948), rutile (Dayal and Appalarasimham 1950/51), ammonium di-hydrogen phosphate (Chapelle 1949), aragonite and calcite (Oke 1936 *a* and *b*) and crystalline argon (Henkel 1955). Particular interest attaches to the calculations on quartz, ice and rutile, since these belong respectively to the trigonal, hexagonal and tetragonal systems, and values of all the independent elastic constants were calculated. The final estimates for the elastic constants are given in table 6, in which the bracketed figures have been obtained from the relation $c_{66}=\frac{1}{2}(c_{11}-c_{12})$ imposed by the symmetry of the material. The values of c_{14} for quartz have also been given a negative sign in accordance with the recommendations of the I.R.E. Standard (1949).

The calculated values for quartz and rutile in table 6 have been obtained by the method described above for diamond, that is by an argument based on the crystal structure, and on force constants derived from Raman effect and infra-red data. Saksena (1944) admits some uncertainty in the calculations for quartz to the extent of giving two sets of calculated constants which differ in some instances by approximately 10%. The values quoted above are those giving the best agreement with experiment, but even so, some of the discrepancies (particularly those for c_{11} and c_{44}) are quite large. There are at present no experimental values for the individual constants of rutile, but the compressibility calculated from the theoretical constants agrees well with the experimental value.

In calculating the elastic constants of ice, Penny (1948) assumed a particular atomic structure, thus reducing the number of atomic

constants to two. These were evaluated from the Young's modulus (9.8×10^{10} dynes/cm²) and Poisson's ratio (0.335) for polycrystalline ice, measured by Northwood (1947). The difference between the calculated and the experimental values (Jona and Scherrer 1952) are of the order of 10%; it is noteworthy that the calculations were made some four years before the values were actually measured.

The theories mentioned above have been used in discussing a variety of problems, including the Cauchy relations (Epstein 1946, Zener 1947 a, Stakgold 1950, Burstein *et al.* 1951, Herpin 1953), the elastic properties of β -brass (Samoilovitch 1944, Zener 1947 b, Isenberg 1951, Jones 1952 a, b); the dependence on concentration of the elastic properties of alloys and binary solid solutions (Orlov 1951, Shibuya 1951, Leigh 1951 b, Aptekhar and Finkelshtein 1951, Jones 1952 b, Neighbours and Smith,

Table 6. Calculated and Observed Elastic Constants of Quartz, Ice and Rutile
Unit= 10^{11} dynes/cm²

Material	Calc. (C) or Obs. (O)	c_{11}	c_{33}	c_{44}	c_{66}	c_{12}	c_{13}	c_{14}	Refer- ence
Quartz	C	11.3	10.5	8.4	(5.87)	-0.44	1.40	-1.59	(1)
	O	8.63	10.63	5.76	(3.97)	0.68	1.28	-1.76	(2)
Ice	C	1.52	1.62	0.32	(0.36)	0.80	0.70	—	(3)
	O	1.38	1.50	0.32	(0.33)	0.71	0.58	—	(4)
Rutile	C	30.0	19	13.2	17.6	17.6	13.6	—	(5)

(1) Saksena (1944); (2) Average values from Hearmon (1952); (3) Penny (1948); (4) Jona and Scherrer (1952); (5) Dayal and Appalarasimham (1950).

1954, Bacon 1955); the effect of interstitial atoms and vacancies on the elastic properties of metals (Dienes 1951); the effect of radiation on the elastic constants (Dienes 1952 a, b, Nabarro 1952), and the behaviour of crystal lattices in shear (Zhdanov and Konusov 1950, Mott 1952).

Laval (1951 a, b, 1954 a, b) has cast doubt on the validity of the generalized Hooke's law (1.11) in its usual form when applied to the static and dynamic elastic properties of crystals, and concludes that if the forces between the atoms are not central, the number of independent elastic constants involved in the most general case is 45 as compared with the usual 21 of Voigt, a number valid only if the forces are central.

Laval's analysis indicates that in the generalized Hooke's law (1.11), the relations $T_{ij}=T_{ji}$, $S_{ij}=S_{ji}$ do not hold. There are therefore nine

components of stress and strain instead of the six dealt with in the Voigt formulation. Le Corre (1953 a, b, c, 1954 a, b, 1955) has extended and developed Laval's approach and has given (1953 c) the complete elastic, piezoelectric and dielectric matrices appropriate to all crystal classes on Laval's assumptions. The existence of nine components of stress and strain means that the scheme (1.13) for contracting the suffixes is no longer applicable; instead we have

for	11	22	33	23	31	12	32	13	21
write	1	2	3	4	5	6	7	8	9.

The Laval stiffnesses are then written N_{pq} ($p, q=1, 2 \dots 9$); Laval (1951 b) showed that for a holosymmetric cubic crystal, there are four independent stiffnesses N_{11} , N_{44} , N_{47} and N_{12} . If the forces are central, $N_{12}=N_{47}$ and there are three independent stiffnesses N_{11} , N_{44} and N_{12} , equivalent to Voigt's c_{11} , c_{44} and c_{12} . Le Corre (1951 a, b, 1954 a, b) has shown that on applying this treatment to quartz, the number of independent stiffnesses is 10: N_{11} , N_{33} , N_{44} , N_{55} , N_{12} , N_{13} , N_{14} , N_{17} , N_{47} , and N_{69} . In dynamic problems, certain of these constants occur in pairs, so that there are eight independent dynamic elastic constants: N_{11} , N_{33} , N_{44} , N_{55} , N_{14} , N_{17} , $N_{12}+N_{69}$, $N_{13}+N_{47}$. In the case of central forces $N_{14}=N_{17}$, $N_{44}=N_{55}=N_{47}$, $N_{69}=\frac{1}{2}(N_{11}-N_{12})$, and the independent constants reduce to those of Voigt: c_{11} , c_{33} , c_{44} , c_{12} , c_{13} , c_{14} . Le Corre has paid special attention to ammonium dihydrogen phosphate (ADP) which possesses the seven dynamic Laval stiffnesses: N_{11} , N_{33} , N_{44} , N_{55} , N_{66} , $N_{12}+N_{69}$, $N_{13}+N_{47}$. Le Corre has carried out measurements on vibrating crystals of ADP and has derived the stiffnesses either from observations on the Lucas-Biquard fringes (1934) or from the Schaefer-Bergmann diffraction figures (I, 102). His results in 10^{11} dynes/cm² are:

$$N_{11}=6.105 \pm 0.015; \quad N_{33}=2.86 \pm 0.14; \quad N_{44}=1.03 \pm 0.06$$

$$N_{55}=0.76 \pm 0.05; \quad N_{66}=0.599 \pm 0.0005$$

$$N_{12}+N_{69}=1.79 \pm 0.03; \quad N_{13}+N_{47}=2.46 \pm 0.18.$$

The average values (Hearmon 1952)) of the Voigt constants, derived from three quite independent, but reasonably concordant sets of measurements are:

$$c_{11}=6.61; \quad c_{33}=3.34; \quad c_{44}=0.858; \quad c_{66}=0.598; \quad c_{12}=0.57; \quad c_{13}=1.94, \\ \text{all} \times 10^{11} \text{ dynes/cm}^2.$$

Now, whether the Laval treatment be true or not, we must have $N_{11}=c_{11}$, $N_{33}=c_{33}$ and it will be seen that le Corre's values for these two constants differ by 10–20% from the average values. The difference between N_{44} and N_{55} , which is a crucial test of the Laval theory, amounts to some 30%, but the significance of this difference is reduced by the existence of the difference between le Corre's values for c_{11} and c_{33} and those of other workers.

The values of the constants N_{44} and N_{55} are derived from measurements on a photograph such as fig. 1(b) due to Zwicker (1946). The Laval treatment predicts that the lengths of the axes of the faint outer diffraction

trace should be in the ratio $\sqrt{(N_{55}/N_{44})}$; if the Voigt treatment is adequate, the ratio should be unity. Although it is difficult to make accurate measurements on the figure, at least as reproduced, the axial ratio in fig. 1 (*b*) appears to be about 1.1 : 1; le Corre obtained from his photographs a ratio of 1.17 : 1. There is evidently some support here for Laval's suggestions, but further work is desirable, preferably on other materials, in order to establish the effect beyond doubt.

An independent theoretical investigation of the same problem was made by Viswanathan (1954, 1955), whose conclusions are similar to those of Laval. Shortly afterwards, Raman and Viswanathan (1955 a, b), abandoning the atomistic approach, reconsidered the basic elastic theory of both isotropic and anisotropic materials. According to these workers (1955 a): "The arguments in the classical theory of elasticity . . . may be summed up briefly as follows: that it is sufficient to consider the case of homogeneous strains; that any homogeneous strain may be analysed into a 'pure strain' and a rotation and that the latter should be ignored in formulating the stress-strain relationships; and finally that the tractive forces assumed to act on elements of area in the solid are so related that no torques tending to rotate the volume-elements of the solid are present."

Each of these arguments is regarded as questionable; in dynamic experiments for instance the strains are necessarily heterogeneous and the internal stress system may involve torques as well as tractive forces. In this case the rotational elements of the strain in addition to the normal strain components, will have to be taken into account. When this is done, Raman and Viswanathan (1955 a) show that an isotropic solid requires three independent constants to specify completely its elastic behaviour, instead of the hitherto accepted two.

In their second paper (1955 b), they derive the complete schemes of elastic coefficients for all crystal classes (as had previously been done by le Corre, 1953 c). They confirm le Corre's findings that, for example in the monoclinic system, there are 25 constants instead of the usual 13; in the orthorhombic system, the respective numbers are 15 and 9. In the cubic system Laval's conclusion (p.335) that there are 4 independent constants is modified to the extent that the number is 5 if the cubic axes are 2-fold, and 4 if the axes are 4-fold.

Raman and Krishnamurti (1955) examined the available results for 16 cubic crystals belonging to classes with 4-fold axes, and found systematic differences between the bulk moduli derived from observed velocities of wave propagation and those measured statically. They interpret the differences as indicating the need for 4 independent constants and have evaluated numerically the value of the 4 constants from the data.

It should be realized that throughout the development the strains are regarded as infinitesimal, and the additional constants which arise are therefore of a different nature from the 'third order' constants discussed in §§1.2 and 2.4. The implications of this new approach have not yet

been fully worked out, but the results evidently involve a radical readjustment of ideas on the elastic constants of both isotropic and anisotropic materials. In particular many hitherto accepted equations, and the presentation of experimental results, would be affected. So far, however, all workers, with the exception of le Corre (1953-4) and Raman and Krishnamurti (1955), have expressed the measurements in terms of the Voigt formulation. There is therefore no alternative, at least for the present, to the continuation of this practice and this formulation is adhered to throughout the remainder of the present paper.

§ 2. EXPERIMENTAL

2.1. *Methods of Measurement*

The emphasis throughout the period under review has been on high frequency methods of measuring the elastic constants. The ultrasonic transmission method of Bhagavantam and Bhimasenachar (I, 9) has been applied to a wide variety of materials by Bhagavantam (1946, 1955), Bhagavantam and Bhimasenachar (1946), Bhagavantam and Seshagiri Rao (1951), Bhagavantam and Sundara Rao (1948), Bhagavantam and Suryanarayana (1947 a), Bhimasenachar (1945 a, b, 1949), Bhimasenachar and Seshagiri Rao (1950), Doraiswami (1947), B. Ramachandra Rao (1945), Seshagiri Rao (1949, 1951), Sundara Rao (1947, 1948 a, b, c, 1949 a, b, c, d, e, 1950 a, b), Sundara Rao and Balakrishnan (1948), and modifications to the original method have been suggested by Bhagavantam and B. Ramachandra Rao (1948) and by B. Ramachandra Rao (1950). The first modification converts the method into one very similar to that of Schaefer-Bergmann (I, 102). This latter method depends on the diffraction of light from vibrating crystals and has been used by Jona and Scherrer (1952), Jona (1950), le Corre (1953 a, b, 1954 a, b), Nomoto (1943, 1948), and Zwicker (1946). Some of the patterns obtained by Zwicker with potassium di-hydrogen phosphate and ammonium di-hydrogen phosphate are reproduced in fig. 1 (Pl. II). The tetragonal nature of these materials is clearly shown; for further details of the method, reference may be made to Bergmann's book (1954) which also contains a selection of additional diffraction photographs.

Resonance methods (I, pp. 433, 436), in which the elastic constants are calculated from the resonant frequencies and dimensions of suitable specimens, have also been widely used (Artman and Thompson 1952, Bantle *et al.* 1946, Barkla and Finlayson 1953, Bechmann 1950, 1951 a, 1952 b, 1953 c, 1954, Bechmann and Ayers 1954, Bond *et al.* 1951, Bradfield 1950, Fine 1953, 1955, Kammer *et al.* 1948, Mason 1946, 1950 a, Mason and Matthias 1952, Pursey and Pyatt 1954, Sutton 1953, Yamamoto 1952), and were, in fact, applied by Mason (1946) to the first determination of all the elastic constants of a monoclinic crystal. It is, of course, essential to identify correctly the modes of vibration, and to

solve mathematically the differential equation governing the vibration, so that the elastic constants can be calculated in terms of the dimensions and frequencies of the specimens. Bechmann (1952 d) classifies the types of vibration as follows :

- (1) Thickness vibrations of plates :
(a) Extensional; (b) Shear.
- (2) Contour vibrations of square plates :
(a) Extensional (3 kinds); (b) Shear.
- (3) Contour vibrations of rectangular plates :
(a) Extensional; (b) Shear.
- (4) Longitudinal vibrations of narrow bars :
(a) Extensional; (b) Flexural; (c) Torsional,
to which (1954) he later adds
- (5) Contour vibrations of circular plates :
(a) Extensional; (b) Torsional.

When the conditions are simple, for example, a long bar vibrating in longitudinal motion, the mathematical solutions can be derived without much trouble (e.g. Mason 1950 a). If, however, the conditions are more complex, for instance, a plate of the material vibrating in a contour or thickness shear mode, the solution is more difficult to obtain. Contributions to the solution of this and allied problems have been made by Bechmann (1951 a, 1952 a, c, d, 1953 d, 1954), Cerná (1951), Eckstein (1945, 1946), Hok (1948), Mähly (1951), Mason (1950 a), Meier and Schuster (1953 b), Mindlin (1951, 1952), Mindlin and Forray (1954) and Mindlin and Deresiewicz (1955). Mähly (1951) has summarized the more formal mathematical aspects of the problem, and convenient general summaries have been given by Bechmann (1952 c, d, 1953 c, 1954). In addition to making mathematical contributions, Mason (1946, 1950 a) and Bechmann (1950, 1951 a, 1952 b) have also measured the frequencies of plates vibrating in these complex modes and have calculated the elastic constants from the results. The production of some of these modes is facilitated by partially silvering the specimens, and investigations of this point of technique have been made by S. Ramachandra Rao (1947), Bechmann and Parsons (1951) and Mindlin and Deresiewicz (1954 b).

A new method which has become popular recently involves the measurement of the transmission velocity of ultrasonic pulses through the material (Arenberg 1950, Bergmann 1954, Bond *et al.* 1951, Bozorth *et al.* 1951, Bradfield 1950, Galt 1948, Gold 1950 a, Huntington 1947, Kammer 1955, Lazarus 1949 a, b, McSkimin 1950, 1953, 1955, Neighbours *et al.* 1952, Northwood 1947, Overton and Swim 1951, Price 1949, Price and Huntington 1950). The transmission velocity is measured by techniques similar to those used in radar, and the effective elastic constant is calculated from the phase velocity, and the density of the specimen.

The method of Bhagavantam and his co-workers also requires the transmission velocities; the analysis is usually made in terms of the Christoffel equations (Love, I, 73, Cady 1946, Bechmann 1952 c, see also Post 1948, Pastori 1949, Musgrave 1954 a, b). These equations involve the six quantities λ_{ab} , where a, b can take the values 1, 2, 3, and $\lambda_{ab} = \lambda_{ba}$. The possible phase velocities v are the roots of

$$\begin{vmatrix} \lambda_{11} - \rho v^2 & \lambda_{12} & \lambda_{13} \\ \lambda_{12} & \lambda_{22} - \rho v^2 & \lambda_{23} \\ \lambda_{13} & \lambda_{23} & \lambda_{33} - \rho v^2 \end{vmatrix} = 0, \quad . \quad . \quad . \quad (2.11)$$

where ρ is the density, and the λ_{ab} are given by

$$\begin{aligned} \lambda_{ab} = & l^2 c_{1a1b} + m^2 c_{2a2b} + n^2 c_{3a3b} \\ & + mn(c_{2a3b} + c_{3a2b}) + nl(c_{3a1b} + c_{1a3b}) + lm(c_{1a2b} + c_{2a1b}), \end{aligned} \quad (2.12)$$

where l, m, n are the direction cosines of the normal to the wave front and the suffixes to the stiffnesses are written out in full. Thus, for example, if $a=1, b=2$, and reverting to the more usual two suffix notation for the stiffnesses,

$$\begin{aligned} \lambda_{12} = & l^2 c_{16} + m^2 c_{26} + n^2 c_{45} \\ & + mn(c_{46} + c_{25}) + nl(c_{14} + c_{56}) + lm(c_{12} + c_{66}), \end{aligned}$$

and similarly for the other λ_{ab} . Specialization of eqns. (2.11) and (2.12) to the various crystal systems has been carried out as follows: monoclinic by Sundara Rao (1949 d); orthorhombic by Huntington (1947), Seshagiri Rao (1951), Sundara Rao (1949 c, 1950, a, b); trigonal by Bhimasenachar (1945 a), Sundara Rao (1949 e); tetragonal by Price and Huntington (1950); hexagonal by Bhimasenachar (1945 b), Gold (1950 a), Musgrave (1954 b); cubic by Bhagavantam and Suryanarayana (I, 10), Huntington (1947) and others. In piezo-electric crystals, the Christoffel equations are modified owing to the interaction between electrical and mechanical effects; these modifications have been discussed by Shaposhnikov (1941), Cotte (1944), Eckstein (1946), Mercier (1949), Kyame (1949, 1954), Cady (1950), and Meier and Schuster (1953 a).

Along the cubic axes [100] in cubic crystals, the velocities of propagation are the roots of

$$\begin{vmatrix} c_{11} - \rho v^2 & 0 & 0 \\ 0 & c_{44} - \rho v^2 & 0 \\ 0 & 0 & c_{44} - \rho v^2 \end{vmatrix} = 0 \quad . \quad . \quad (2.13)$$

and there is therefore one longitudinal velocity $v_1 = (c_{11}/\rho)^{1/2}$ and two identical shear velocities $v_2 = v_3 = (c_{44}/\rho)^{1/2}$. Along a face diagonal [110] the determinant becomes

$$\begin{vmatrix} [\frac{1}{2}(c_{11} + c_{12}) + c_{44}] - \rho v^2 & 0 & 0 \\ 0 & \frac{1}{2}(c_{11} - c_{12}) - \rho v^2 & 0 \\ 0 & 0 & c_{44} - \rho v^2 \end{vmatrix} = 0 \quad (2.14)$$

and the velocities are: one longitudinal, $v_1 = \{[\frac{1}{2}(c_{11} + c_{12}) + c_{44}]/\rho\}^{1/2}$ and two shear, $v_2 = [\frac{1}{2}(c_{11} - c_{12})/\rho]^{1/2}$ and $v_3 = (c_{44}/\rho)^{1/2}$.

In eqns. (2.13) and (2.14) the three modes are independent, and can be identified as purely longitudinal or purely transverse. In general, however, this is not so, and the particular directions in which the propagation is purely longitudinal have been investigated by Borgnis (1955) for materials belonging to the trigonal, hexagonal, tetragonal and cubic systems. Borgnis finds, for example, that in α -quartz, there are five such distinct directions, not counting the ones which are equivalent by symmetry properties.

It should be noted that by measuring the three velocities in the [110] direction, it is possible to derive the three independent constants of cubic materials from observations on a single specimen. However, the use of additional specimens enables the results to be checked and hence established with greater certainty. The early workers with the pulse transmission technique used simple orientations such as those discussed above, but this procedure entails either cutting or growing the specimens in the required orientation. In his work on silver chloride, Arenberg (1950) used a crystal of arbitrary, but known orientation, and obtained his elastic constants from approximate equations. This question has been further considered by Neighbours and Smith (1950), and Neighbours *et al.* (1952), who have shown that the velocities for a cubic crystal are the roots of

$$\begin{vmatrix} c_{11}' - \rho v^2 & c_{16}' & c_{15}' \\ c_{16}' & c_{66}' - \rho v^2 & c_{56}' \\ c_{15}' & c_{56}' & c_{55}' - \rho v^2 \end{vmatrix} = 0 \quad . \quad (2.15)$$

where the primes indicate that the stiffnesses are transformed to the arbitrary orientation. The occurrence of off-diagonal terms in (2.15) means that the modes are coupled, and that it is not possible to get exact expressions for the velocities, but Neighbours *et al.* apply a perturbation method to obtain values of c_{11} , c_{12} and c_{44} by a successive approximation procedure. More recently, the method has been extended by Neighbours (1954) to crystals belonging to the hexagonal, tetragonal and orthorhombic systems. Other matters associated with wave propagation in cubic crystals have been considered by Mapleton (1952, reflection); Fein and Smith (1952, polarization) and de Klerk and Musgrave (1955, internal conical refraction).

Another method, developed by Ramachandran and Wooster (1951 a, b) depends on entirely new principles. Owing to the existence of the acoustic wave spectrum in crystals (Born and Huang 1954), the x-ray diffraction photographs show diffuse spots whose positions differ from those of the ordinary Bragg reflections. Ramachandran and Wooster have shown how these diffuse reflections can be used to determine the elastic constants. The technique is difficult and consequently the method is not highly accurate at present, but Ramachandran and Wooster have succeeded in measuring the stiffness constants of KBr, KCl, NaClO₃, galena and

hexamethylene tetramine. The method has also been applied by Prince and Wooster to measuring the elastic constants of zinc blende (1951) and diamond (1953); by Hoerni and Wooster (1952) to lithium fluoride; by Prasad & Wooster (1955 a, c) to silicon and tin; and by Jacobsen (1955) to copper. Sometimes, the emphasis is shifted, and the known elastic constants are applied in determining the acoustic spectrum from the diffuse reflections. This approach has been used by Olmer (1948) for aluminium; by Curien (1952, 1954) for α -iron and sodium; by Cole and Warren (1952) for β -brass; by Cole (1953) for silver chloride; and by Joynson (1954) for zinc. A general review of diffuse x-ray scattering has been published by Wooster (1954), and the application of the method to non-cubic crystals has been considered by Prasad and Wooster (1955 b).

Another effect which depends on the existence of the acoustic wave spectrum in crystals is the Brillouin scattering. Brillouin (1922) showed that the Doppler interaction between light and the acoustic waves leads to the production of light components shifted in frequency by an amount

$$\Delta v = \pm 2\nu\mu \frac{v}{c} \sin \frac{\theta}{2}, \quad . \quad . \quad . \quad . \quad . \quad (2.16)$$

where v , μ , ν , c and θ are respectively the frequency of the incident radiation, the refractive index of the medium, the velocity of sound in the medium, the velocity of light *in vacuo* and the angle of scattering. Krishnan (1947 a, b) has used a high resolution spectrometer to measure the frequency shifts of the Brillouin lines accompanying the Raman lines of diamond and alumina; similar measurements have been made by Krishnan and Chandrasekharan (1950) on quartz and by Chandrasekharan (1950 a), also on diamond. Chandrasekharan (1950 b, 1951, 1953) has discussed the scattering in birefringent crystals and has shown that there are 12 pairs of Doppler components as contrasted with 3 pairs for optically isotropic substances. It is evident from eqn. (2.16) that ν can be calculated from the measured, or known values of $\Delta\nu$, ν , μ , c and θ and hence the effect offers in principle, a method of measuring the elastic constants. Although no actual values of the fundamental elastic constants determined by this method have yet been reported, Krishnan (1955) has compared the effective stiffnesses in various directions in LiF, NaCl, KCl, diamond, quartz, calcite, alumina and barytes as measured by the method, with the corresponding quantities calculated from the known elastic constants, and has obtained reasonable agreement. The frequency shifts are very small and need a high resolution spectrograph for their measurement; in laboratories possessing the necessary equipment the method may prove to be a valuable adjunct to other methods.

X-rays have also been used by Günther (1941) to measure the elastic constant of aluminium monocrystals but this application is quite distinct both in principle and in practice from that of Ramachandran and Wooster. Günther, in fact, used x-ray diffraction to measure the dimensional changes produced by stress, and the elastic constants were then calculated from the ratio of applied stress to measured strain. Günther's work

was an early example in the field of measuring strain by x-ray diffraction ; more recent work on this problem is discussed by Greenough (1955) and Hershey (1954). The method is essentially a static one, as opposed to the dynamic methods so far discussed. The popularity of static methods has declined recently, but nevertheless, the constants of α -brass (Fenn *et al.* 1950) and of nickel and cobalt (Honda and Shirakawa 1949) have been determined wholly by static methods. The measurements on α -brass are interesting because the extensional strains were measured with electric resistance strain gauges, the first time this technique of strain measurement has been applied to single crystals (see however § 2.2). In their work on β -brass, Artman and Thompson (1952) used static torsion for measuring the rigidity moduli. They also measured the bending which normally accompanies the torsion, and found good agreement between the observed and the theoretical values.

Hearmon and Adams (1952) have suggested methods of estimating the elastic constants which depend on the deflection of plates under the influence of torsional and bending moments, and have used these methods in a study of the elastic behaviour of plywood. The methods in their present form require plates of rather large size, but if plates of suitable size were available, or if suitable micro-methods could be developed, the application of the methods to crystalline materials would be of considerable interest, because with their aid, compliances such as s_{16} and s_{26} , which determine the magnitude of the torsion-flexure and shear-extension coupling, can be determined directly.

Finally, Kleber (1945, 1950) has suggested the application of a low frequency coupled pendulum method to the determination of the elastic constants of crystals, but no actual measurements by this method appear to have been carried out so far.

2.2. Results

The experimental results are collected in tables 7A-G. Nearly all have been published in the period 1945-55, although some earlier results, which were overlooked in the preparation of I, have been included. Some of the methods now in common use yield the stiffnesses directly, whereas others yield the compliances. The original authors do not always give both sets of constants and in such cases the results have been converted by the writer, using the conversion equations appropriate to the crystal system to which the material belongs (Cady 1946, Voigt I, 115, Zwicker 1946 etc.). All of the results refer to 'room' temperature (c. 20-30°C) unless otherwise stated. As discussed in § 2.6 the values of the elastic constants of piezo-electric materials theoretically depend on the electrical conditions prevailing during their measurement, but the differences due to these causes at ordinary temperatures are usually small, except in the s_{44} and c_{44} constants of Rochelle salt and the s_{66} and c_{66} constants of ammonium di-hydrogen phosphate.

Measured values of elastic constants obtained before 1944 will in general be found in I, table 5, and will not be quoted again here. If, however, earlier results are available in I for material included in table 7, this fact is indicated by an asterisk (*). The units are 10^{-13} cm²/dyne for s and 10^{11} dyne/cm² for c .

Tables 7A to 7G. Experimental Values of Elastic Constants

Table 7A. Cubic System. Elements and Alloys

Material	s_{11}	s_{44}	s_{12}	c_{11}	c_{44}	c_{12}	Reference
Aluminium*	17.4	35.1	— 6.6	10.56	2.85	6.39	Lazarus (1949 a)
Aluminium 20°C	15.7	35.9	— 5.8	11.2	2.79	6.6	Sutton (1953)
β -Brass (51.1% Cu)	36.4	12.2	—16.8	12.79	8.22	10.91	Lazarus (1949 b)
β -Brass (55.1% Cu)	41.05	13.44	—18.98	11.9	7.4	10.2	Artman and Thompson (1952)
Copper*	14.95	13.23	— 6.28	17.1	7.56	12.4	Lazarus (1949 a)
Copper	15.3	15.5	— 6.5	17.0	6.45	12.4	Jacobsen (1955)
Copper	15.0	13.26	— 6.3	16.8	7.54	12.1	Overton and Gaffney (1955)
CuZn (4.59% Zn)	15.91	13.48	— 6.71	16.34	7.42	11.92	Neighbours and Smith (1954)
CuAl (4.81% Al)	15.90	13.35	— 6.73	16.58	7.49	12.16	
CuAl (9.98% Al)	16.75	13.05	— 7.11	15.95	7.66	11.76	
CuGa (1.58% Ga)	15.38	13.46	— 6.45	16.50	7.43	11.92	
CuGa (4.15% Ga)	15.91	13.50	— 6.73	16.52	7.41	12.10	
CuSi (4.17% Si)	16.10	13.37	— 6.85	16.78	7.48	12.42	
CuSi (5.16% Si)	16.71	13.35	— 7.10	16.08	7.49	11.88	
CuSi (7.69% Si)	17.72	13.50	— 7.66	16.58	7.41	12.64	
CuGe (1.03% Ge)	15.44	13.33	— 6.50	16.66	7.50	12.10	
CuGe (1.71% Ge)	15.72	13.33	— 6.60	16.31	7.50	11.82	
Germanium 20°C	9.78	14.90	— 2.66	12.89	6.71	4.83	McSkimin (1953)
Germanium 25°C	9.68	14.94	— 2.70	13.16	6.69	5.09	Fine (1953)
Molybdenum	2.8	9.1	— 0.78	45.5	11.0	17.6	Druyvesteyn (1941)
Nickel	8.35	9.8	— 3.28	24.4	10.2	15.8	Yamamoto (1950)
Nickel	7.24	9.56	— 2.72	25.2	10.4	15.1	Honda and Shirakawa (1949)
Nickel	7.67	8.24	— 2.95	25.12	12.13	15.71	Bozorth <i>et al.</i> (1951)
Nickel	7.69	8.36	— 2.92	24.36	11.96	14.94	de Klerk and Musgrave (1955)
Nickel†	7.50	8.16	— 2.86	25.26	12.26	15.61	Bozorth <i>et al.</i> (1951)
Nickel†	7.21	8.08	— 2.71	25.28	12.38	15.2	Neighbours <i>et al.</i> (1952)
Nickel†	7.34	8.02	— 2.74	24.65	12.47	14.73	de Klerk and Musgrave (1955)
Silicon 20°C	7.69	12.56	— 2.14	16.57	7.96	6.39	McSkimin (1953)
Silicon	7.65	11.9	— 2.16	16.8	8.4	6.6	Prasad and Wooster (1955 a)
Silver*	22.88	21.68	— 9.83	12.40	4.61	9.34	Bacon (1955)
AgMg (3.07% Mg)	23.37	21.74	—10.01	11.98	4.60	8.98	
AgMg (7.33% Mg)	23.94	22.10	—10.24	11.59	4.52	8.66	
AgZn (2.40% Zn)	23.89	21.85	—10.30	12.09	4.58	9.16	
AgZn (3.53% Zn)	23.54	21.68	—10.16	12.30	4.61	9.33	
AgCd (1.34% Cd)	23.07	21.69	— 9.91	12.28	4.61	9.25	
AgCd (1.92% Cd)	23.10	21.77	— 9.91	12.16	4.59	9.13	
AgIn (8.36% In)	25.30	22.20	—10.95	11.66	4.50	8.90	
AgSn (3.17% Sn)	24.29	21.83	—10.51	12.10	4.58	9.22	
AgPd (6.22% Pd)	21.93	20.79	— 9.40	12.77	4.81	9.58	

† Saturated magnetically.

The composition of copper and silver alloys is expressed in atomic per cent.

The previous results for diamond (I, 8) and galena (I, 9) have been superseded (Bhagavantam and Bhimasenachar 1946, Bhagavantam and Seshagiri Rao 1951). The values obtained by Fenn *et al.* (1950) on α -brass, and by Lutz *et al.* (1950) and Chapelle (1951) on ammonium di-hydrogen arsenate have not been included in table 7. In both cases, the authors express the results as compliances, but in converting to stiffnesses,

Material	s_{11}	s_{44}	s_{12}	c_{11}	c_{44}	c_{12}	Reference
Alum (K) *	52.5	119	-15.6	2.54	0.84	1.07	Bhagavantam and B. Ramachandra Rao (1948)
Alum (K)	52	118	-15	2.56	0.85	1.07	B. Ramachandra Rao (1950)
Alum (K) 100% K	51.8	116	-15.3	2.56	0.86	1.07	
Alum (K-Cr) 86.5% K	52.5	123	-15.4	2.52	0.81	1.05	
Alum (K-Cr) 60% K	53.1	128	-15.4	2.47	0.78	1.01	
Alum (K-Cr) 54.5% K	53.8	128	-15.6	2.44	0.78	1.00	Sundara Rao (1947)
Alum (Cr) 0% K	54.1	130	-15.3	2.37	0.77	0.93	
Alum (NH ₄)	53.5	125	-15.9	2.50	0.80	1.06	Sundara Rao (1948 c)
Alum (NH ₄)	53.8	123	-16.2	2.51	0.81	1.08	Sundara Rao (1948 c)
Alum (Ti)	48	115	-15	2.9	0.87	1.3	Bhagavantam (1955)
Ammonium Bromide †	36.2	189	-6.0	2.96	0.53	0.59	Sundara Rao and Balakrishnan (1948)
Ammonium Chloride	27.2	147	-4.2	3.90	0.68	0.72	Sundara Rao and Balakrishnan (1948)
Barium Nitrate	19.5	82.6	-4.6	6.02	1.21	1.86	Bhagavantam and Sundara Rao (1948)
Barium Nitrate	19.4	82.0	-4.6	6.04	1.22	1.86	Sundara Rao (1948 c)
Barium Nitrate	19.9	82.6	-4.8	5.93	1.21	1.89	Bhimasenachar and Seshagiri Rao (1950)
Chromite	4.27	8.57	-1.32	32.25	11.67	14.37	Doraiswami (1947)
Cobalt Zinc Ferrite 30°C	6.49	12.8	-2.37	26.6	7.8	15.3	McSkimin <i>et al.</i> (1954)
Diamond*	1.38	2.32	-0.40	95	43	39	Bhagavantam and Bhimasenachar (1946)
Diamond 300°C	1.05	2.3	-0.24	110	44	33	Prince and Wooster (1953)
Fluorspar*	7.10	28.8	-1.66	16.44	3.47	5.02	Bhagavantam (1946)
Galena*	12	40	-3	10.2	2.5	3.8	Ramachandran and Wooster (1951 b)
Galena	8.7	40.3	-1.64	12.70	2.48	2.98	Bhagavantam and Seshagiri Rao (1951)
Garnet 21.8% FeO	7.11	17.5	-2.2	19.7	5.7	9.0	B. Ramachandra Rao (1945)
Garnet 22.7% FeO	8.02	16.9	-2.7	19.2	5.9	9.9	
Garnet 23.6% FeO	7.03	14.9	-2.3	21.0	6.7	10.3	
Garnet 23.0% FeO	6.42	14.3	-2.1	22.2	7.0	10.4	
Garnet 26.2% FeO	7.36	16.1	-2.6	22.6	6.2	12.6	
Garnet 28.7% FeO	6.32	14.7	-2.3	27.3	6.8	15.7	
Garnet 33.5% FeO	3.87	11.2	-1.1	32.7	8.9	12.4	Ramachandran and Wooster (1951 b)
Hexamethylene Tetramine	70	140	-12	1.5	0.7	0.3	

Lithium Fluoride*	13.6	18.0	—	4.0	9.74	5.54	4.04	Rao (1950)
Lithium Fluoride	10.7	18.5	—	2.97	11.9	5.42	4.58	Huntington (1947)
Lithium Fluoride	11.7	18.7	—	3.64	11.9	5.34	5.38	Sundara Rao (1949 b)
Lithium Fluoride	13.7	18.5	—	4.1	9.9	5.4	4.3	Seshagiri Rao (1949)
Magnesium Oxide*	4.08	6.76	—	0.95	28.6	14.8	8.7	Hoerni and Wooster (1952)
Magnetite	4.59	10.47	—	1.26	27.5	9.55	10.4	Bhagavantam (1955)
Magnetite	4.80	10.13	—	1.37	27.0	9.87	10.8	Doraiswami (1947)
Potassium Bromide*	30.3	197	—	4.1	3.45	0.508	0.54	Huntington (1947)
Potassium Bromide	30.4	198	—	4.36	3.46	0.505	0.58	Galt (1948)
Potassium Bromide	27	160	—	4	3.8	0.64	0.60	Ramachandran and Wooster (1951 b)
Potassium Chloride*	26.2	160	—	3.5	3.98	0.625	0.62	Galt (1948)
Potassium Chloride	25	130	—	4	4.3	0.79	0.75	Ramachandran and Wooster (1951 b)
Potassium Chloride	25.7	159	—	3.8	4.095	0.630	0.705	Lazarus (1949 a)
Pyrites*	2.87	9.50	+	0.42	36.2	10.52	—	Bhagavantam (1946)
Pyrites	2.86	9.22	+	0.40	36.16	10.84	—	
Pyrites	2.94	9.66	+	0.51	35.85	10.35	—	
Pyrites	2.89	9.22	+	0.41	35.78	10.85	—	
Pyrites	2.77	9.86	+	0.41	37.51	10.14	—	
Silver Bromide	31.2	137	—	11.5	5.62	0.728	3.28	Tannhauser and Lawson (1954)
Silver Chloride	30.4	160	—	11.4	6.01	0.625	3.62	Arenberg (1950)
Sodium Bromide*	28.7	103	—	5.8	3.87	0.97	0.97	Bhagavantam (1955)
Sodium Chloride*	22.9	79.4	—	4.65	4.87	1.26	1.24	Galt (1948)
Sodium Chloride	22.5	78.7	—	4.57	4.97	1.27	1.27	Bhagavantam (1946)
Sodium Chloride	23.0	79.0	—	4.7	4.85	1.265	1.23	Huntington (1947)
Sodium Chloride	22.6	77.9	—	4.5	4.911	1.284	1.225	Lazarus (1949 a)
Sodium Chloride 17°C	23.01	78.41	—	4.73	4.864	1.275	1.258	Overton and Swim (1951)
Strontium Nitrate	29.8	68.5	—	9.4	4.73	1.46	2.18	Bhimasenachar and Seshagiri Rao (1950).
Thallium Bromide	33.9	132	—	9.5	3.78	0.756	1.48	
Thallium Bromide	33.1	136	—	9.2	3.85	0.737	1.49	
Thallium Bromide Chloride	39.1	173	—	11.1	3.31	0.579	1.32	Arenberg (1948-9).
Thallium Bromide Iodide	37	180	—	11	3.6	0.555	1.5	Krasnov and Stepanov (1953)
Thallium Bromide Iodide †	31.6	132	—	8.7	4.01	0.760	1.53	Arenberg (1948-9)
Thallium Chloride	20.5	29.4	—	8.1	10.0	3.4	6.5	Prince & Wooster (1951)

Material	Suffixes					Reference
	11	33	44	12	13	
Apatite	$\begin{Bmatrix} s_{pq} \\ c_{pq} \end{Bmatrix}$ 7.49 † 16.67	10.9 13.96	15.1 6.63	0.97 † 1.31	— 4.0 6.55	{ Bhimasenachar (1945 b)
Beryl I*	$\begin{Bmatrix} s_{pq} \\ c_{pq} \end{Bmatrix}$ 4.27 27.81	4.47 24.8	15.1 6.61	— 1.35 10.01	— 0.80 6.77	{ B. Ramachandra Rao ‡
Beryl II	$\begin{Bmatrix} s_{pq} \\ c_{pq} \end{Bmatrix}$ 3.97 29.71	4.21 26.5	13.3 7.54	— 1.17 10.26	— 0.78 7.39	{ B. Ramachandra Rao ‡
Beryl I	$\begin{Bmatrix} s_{pq} \\ c_{pq} \end{Bmatrix}$ 4.22 28.00	4.46 24.8	15.2 6.58	— 1.30 9.9	— 0.79 6.70	{ Sundara Rao (1948 c)
Beryl II	$\begin{Bmatrix} s_{pq} \\ c_{pq} \end{Bmatrix}$ 4.12 28.73	4.67 24.18	14.3 7.02	— 1.20 9.91	— 0.88 7.29	{ Sundara Rao (1948 c)
Beryllium	$\begin{Bmatrix} s_{pq} \\ c_{pq} \end{Bmatrix}$ 3.77 30.8	3.37 35.7	9.09 11.0	1.04 — 5.8	— 1.17 8.7	{ Gold (1950 a)
Cobalt	$\begin{Bmatrix} s_{pq} \\ c_{pq} \end{Bmatrix}$ 6.22 26.3	5.08 28.3	19.3 5.2	— 2.77 15.2	— 1.63 13.3	{ Honda and Shirakawa (1949)
Cobalt	$\begin{Bmatrix} s_{pq} \\ c_{pq} \end{Bmatrix}$ 4.73 30.7	3.19 35.81	13.24 7.55	— 2.31 16.50	— 0.69 10.27	{ McSkimin (1955)
Ice —16°C	$\begin{Bmatrix} s_{pq} \\ c_{pq} \end{Bmatrix}$ 104 1.385	85 1.499	314 0.319	—43 0.707	—24 0.581	{ Jona and Scherrer (1952)
β-Quartz* 600°C	$\begin{Bmatrix} s_{pq} \\ c_{pq} \end{Bmatrix}$ 9.41 11.66	10.62 11.04	27.73 3.606	— 0.60 1.67	— 2.62 3.28	{ Kammer, Pardue and Frissell (1948)
Zinc*	$\begin{Bmatrix} s_{pq} \\ c_{pq} \end{Bmatrix}$ 8.38 16.11	28.4 6.11	26.1 3.83	0.5 3.42	— 7.31 5.03	{ Wert and Tyndall (1949)

† These values differ from those given by Bhimasenachar, who appears to have made an error in the conversions.

‡ Quoted by Sundara Rao (1948 c).

Table 7D. Tetragonal System

Material	Suffixes					Reference
	11	33	44	66	12	13
Ammonium di-hydrogen phosphate (deuterated) 20°C	19	44	110 §	163 §	4	-11
	6.2	3.0	0.91	0.61	-0.5	1.4
Nickel Sulphate $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	65	34.3	86.5 §	56.2 §	-46.8	-1.3
	3.21	2.93	1.16	1.78	2.31	0.21
Potassium di-hydrogen arsenate	19	27	86 §	152 §	2	1
	5.3	3.7	1.2	0.7	-0.6	-0.2
Potassium di-hydrogen phosphate 7°C†	16	19	74	158	-2	-5.5
	7.4	6.8	1.35	0.63	1.8	2.7
Tin*	14.6	8.5	20.6	19.0	-5.3	-2.07
	8.6	13.3	4.9	5.3	3.5	3.0
Zircon	13.9	22.1	72	62	-1.6	1.4
	7.35	4.60	1.38	1.60	0.90	-0.54

† Quoted by van Dyke and Gordon (1950).

‡ Ammonium di-hydrogen phosphate and other values for potassium di-hydrogen phosphate, see table 11 and Hearnon (1952).

§ Denotes zero or constant field (see §2.6).

Table 7E. Trigonal System

Material	Suffixes					Reference
	11	33	44	12	13	14
Alumina (Corundum)	2.84	2.21	5.47	— 0.95	— 0.47	— 1.52
Alumina	46.6	50.6	23.5	12.7	11.7	9.4
(Corundum)	2.90	1.94	5.78	— 1.05	— 0.38	— 1.71
Aluminium	46.5	56.3	23.3	12.4	11.7	10.1
Phosphate	16.1 §	16.1 §	53 §	— 0.1 §	— 8.3 §	8.9 §
Phosphate	10.5	13.4	2.31	2.93	6.93	— 1.27
Calcespar *	11.0	17.3	39.4	— 3.4	— 4.3	— 8.6
Calcespar *	13.74	8.01	3.42	4.40	4.50	— 2.03
Dextrose	56.9 §	52.3	158 §	— 8.6 §	— 16.0	— 3.4 §
Sodium Bromide	2.06	2.40	0.634	0.53	0.79	0.03
Dextrose	63.8 §	70.2	130 §	— 26.1 §	— 16	3.6 §
Sodium Chloride	2.20	1.77	0.771	1.09	0.75	— 0.03
Dextrose	60.2 §	51.6	130 §	— 34.3 §	— 6.2	3.8 §
Sodium Iodide	2.58	2.06	0.771	1.52	0.49	— 0.03
Mercury	154	45	151	— 119	— 21	— 100
—190°C	3.60	5.05	1.29	2.89	3.03	0.47
Sodium	13.4	30.8	51.5	— 2.2	— 4.8	— 6.0
Nitrate	8.67	3.74	2.13	1.63	1.60	— 0.82
Tourmaline*	3.85	6.36	15.4	— 0.48	— 0.71	0.45
Tourmaline I	27.2	16.5	6.5	4.0	3.5	— 0.68
Tourmaline I	4.22	7.34	17.1	— 0.80	— 1.11	0.76
Tourmaline I	26.3	15.1	5.95	6.1	4.9	— 0.9
Tourmaline II	3.64	5.89	15.4	— 1.00	— 0.53	— 0.29
Tourmaline II	30.4	17.6	6.5	8.8	3.5	— 0.4

Tourmaline* see also table 11.

Quartz* see table 11 and Hearmon (1952).

§ Denotes zero or constant field (see § 2.6).

Table 7F. Orthorhombic System

Material	Suffixes								Reference
	11	22	33	44	55	66	12	13	23
Barytes* (BaSO ₄) $\begin{Bmatrix} s_{pq} \\ c_{pq} \end{Bmatrix}$	18.40 8.62	17.36 9.17	10.96 10.84	83.33 1.20	34.84 2.87	36.50 2.74	— 9.45 5.23	— 2.68 3.41	— 2.73 3.56
Celestite (SrSO ₄) $\begin{Bmatrix} s_{pq} \\ c_{pq} \end{Bmatrix}$	21.97 10.44	21.85 10.61	11.42 12.86	74.08 1.35	35.84 2.79	37.59 2.66	— 13.87 7.73	— 3.66 6.05	— 4.00 6.19
Iodic Acid $\begin{Bmatrix} s_{pq} \\ c_{pq} \end{Bmatrix}$	39.8 3.03	20.1 5.45	25.6 4.36	54.5 § 1.84	45.6 § 2.19	57.6 § 1.74	— 7.75 1.19	— 9.7 1.17	— 0.45 0.55
Lithium Ammonium Tartrate $\begin{Bmatrix} s_{pq} \\ c_{pq} \end{Bmatrix}$	30 3.86	25.6 5.39	35 3.63	84 § 1.19	150 § 0.67	43 § 2.33	— 8.2 1.65	— 2.7 0.87	— 12.2 2.01
Magnesium Sulphate MgSO ₄ ·7H ₂ O $\begin{Bmatrix} s_{pq} \\ c_{pq} \end{Bmatrix}$	24.5 6.98	34.1 5.29	15.0 8.22	93.5 1.07	42.9 2.33	45.0 2.22	— 16.6 3.90	— 2.68 2.82	— 6.05 2.83
Sodium Ammonium Tartrate* $\begin{Bmatrix} s_{pq} \\ c_{pq} \end{Bmatrix}$	57.0 3.68	38.5 5.09	40 5.54	94.5 § 1.06	330 § 0.303	115 § 0.87	— 15.5 2.72	— 22 3.08	— 15.5 3.47
Sodium Tartrate $\begin{Bmatrix} s_{pq} \\ c_{pq} \end{Bmatrix}$	37.1 4.61	31.6 5.47	26.4 6.65	80.6 1.24	323 0.31	102 0.98	— 12.0 2.86	— 11.5 3.20	— 10.9 3.52
Strontium Formate $\begin{Bmatrix} s_{pq} \\ c_{pq} \end{Bmatrix}$	28.4 4.39	31 3.48	31 3.74	65 § 1.54	93 § 1.07	58 § 1.72	— 8 1.04	+11 — 1.49	— 2 — 0.14
Sulphur $\begin{Bmatrix} s_{pq} \\ c_{pq} \end{Bmatrix}$	71 2.40	83 2.05	30 4.83	232 0.43	115 0.87	132 0.76	— 36 1.33	— 13 1.71	— 15 1.59
Zinc Sulphate ZnSO ₄ ·7H ₂ O $\begin{Bmatrix} s_{pq} \\ c_{pq} \end{Bmatrix}$	29.5 4.00	37.7 3.22	20.4 5.45	200 0.50	58.8 1.70	55.3 1.81	— 10.8 1.32	— 3.49 1.08	— 6.10 1.19

Rochelle Salt see table 11 and Hearmon (1952).

§ Denotes zero or constant field.

Table 7G. Monoclinic System

Material	Suffixes													Reference
	11	22	33	44	55	66	12	13	23	15	25	35	46	
Di-potassium tartrate (DKT)	$\begin{Bmatrix} spq \\ \dagger \\ \ddagger \\ \S \end{Bmatrix}$ 22.4 47.5 38.9	$\begin{Bmatrix} 33.7 \\ 35.3 \\ 33.7 \end{Bmatrix}$	$\begin{Bmatrix} 38.6 \\ 24.0 \\ 22.6 \end{Bmatrix}$	$\begin{Bmatrix} 119 \\ 113.5 \\ 104.3 \end{Bmatrix}$	$\begin{Bmatrix} 81.5 \\ 102 \\ 81.7 \end{Bmatrix}$	$\begin{Bmatrix} 104.1 \\ 122.5 \\ 119.2 \end{Bmatrix}$	$\begin{Bmatrix} -0.8 \\ -17.4 \\ -10.6 \end{Bmatrix}$	$\begin{Bmatrix} -16.4 \\ -8 \\ -16.4 \end{Bmatrix}$	$\begin{Bmatrix} -10.5 \\ -6.2 \\ -0.7 \end{Bmatrix}$	$\begin{Bmatrix} -6.4 \\ -7.5 \\ 8.5 \end{Bmatrix}$	$\begin{Bmatrix} -5.7 \\ 8.0 \\ 5.4 \end{Bmatrix}$	$\begin{Bmatrix} 9.0 \\ -14.0 \\ -6.5 \end{Bmatrix}$	$\begin{Bmatrix} 5.7 \\ -6.8 \\ 5.5 \end{Bmatrix}$	Mason (1950 a) Bechmann and Ayers (1954)
Ethylene diamine tartrate (EDT)	$\begin{Bmatrix} spq \\ spq \end{Bmatrix}$ 39 33.4	$\begin{Bmatrix} 36 \\ 36.5 \end{Bmatrix}$	$\begin{Bmatrix} 98 \\ 100 \end{Bmatrix}$	$\begin{Bmatrix} 187 \\ 192 \end{Bmatrix}$	$\begin{Bmatrix} 172 \\ 117 \end{Bmatrix}$	$\begin{Bmatrix} 174 \\ 191 \end{Bmatrix}$	$\begin{Bmatrix} 2 \\ 3 \end{Bmatrix}$	$\begin{Bmatrix} -52 \\ -30 \end{Bmatrix}$	$\begin{Bmatrix} -18 \\ -18 \end{Bmatrix}$	$\begin{Bmatrix} -5 \\ -17 \end{Bmatrix}$	$\begin{Bmatrix} 2 \\ 15 \end{Bmatrix}$	$\begin{Bmatrix} -25 \\ -26.5 \end{Bmatrix}$	$\begin{Bmatrix} -2 \\ 3.8 \end{Bmatrix}$	Mason (1950 a) Bechmann (1950)
Lithium Sulphate † Lithium Sulphate ‡ Lithium Sulphate §	$\begin{Bmatrix} spq \\ spq \\ spq \end{Bmatrix}$ 23.9 22.9 22.5	$\begin{Bmatrix} 21.3 \\ 22.5 \\ 21.3 \end{Bmatrix}$	$\begin{Bmatrix} 23.1 \\ 22.8 \\ 18.8 \end{Bmatrix}$	$\begin{Bmatrix} 36.9 \\ 71.3 \\ 73.1 \end{Bmatrix}$	$\begin{Bmatrix} 41 \\ 64.0 \\ 52.3 \end{Bmatrix}$	$\begin{Bmatrix} 74 \\ 36.1 \\ 37.9 \end{Bmatrix}$	$\begin{Bmatrix} -9.5 \\ -5.4 \\ -7.5 \end{Bmatrix}$	$\begin{Bmatrix} -5 \\ -7.5 \\ -2.2 \end{Bmatrix}$	$\begin{Bmatrix} -3.6 \\ -4.6 \\ -5.6 \end{Bmatrix}$	$\begin{Bmatrix} 7.1 \\ -2.1 \\ -1.6 \end{Bmatrix}$	$\begin{Bmatrix} -12 \\ -8.3 \\ -13.2 \end{Bmatrix}$	$\begin{Bmatrix} 0.5 \\ 6.3 \\ 8.3 \end{Bmatrix}$	$\begin{Bmatrix} -4.1 \\ 1.4 \\ 7.2 \end{Bmatrix}$	Mason (1950 a) Bechmann (1952 b)
Sodium Thio-sulphate	$\begin{Bmatrix} spq \\ cpq \end{Bmatrix}$ 50.2 3.31	$\begin{Bmatrix} 156 \\ 3.02 \end{Bmatrix}$	$\begin{Bmatrix} 67.4 \\ 4.57 \end{Bmatrix}$	$\begin{Bmatrix} 223 \\ 0.57 \end{Bmatrix}$	$\begin{Bmatrix} 327 \\ 1.11 \end{Bmatrix}$	$\begin{Bmatrix} 212 \\ 0.60 \end{Bmatrix}$	$\begin{Bmatrix} -32.3 \\ 1.83 \end{Bmatrix}$	$\begin{Bmatrix} -6.21 \\ 1.84 \end{Bmatrix}$	$\begin{Bmatrix} -71.9 \\ 1.68 \end{Bmatrix}$	$\begin{Bmatrix} 15.2 \\ 0.25 \end{Bmatrix}$	$\begin{Bmatrix} -182 \\ 1.04 \end{Bmatrix}$	$\begin{Bmatrix} 110 \\ -0.69 \end{Bmatrix}$	$\begin{Bmatrix} 100 \\ -0.27 \end{Bmatrix}$	Sundara Rao (1949 d)
Tartaric Acid	$\begin{Bmatrix} spq \end{Bmatrix}$ 21.6	77	38.5	126	175	96.2	-6.1	-15	-18	28	27.6	-29	-16.4	Mason (1950 a)

† Referred to Mason's axes.

‡ Referred to Bechmann's axes.

§ Mason's values transformed to Bechmann's axes.

|| Sundara Rao's axes transformed $x \rightarrow x_z, y \rightarrow x_y, z \rightarrow y_z$.

For ckt of DKT, EDT, Tartaric Acid and Lithium Sulphate, see table 11.

difficulties are encountered which throw some doubt on the measurements. The compliances given by Fenn *et al.* for one of their specimens (71.2% Cu) are such that the value of c_{11} turns out to be -414×10^{11} . For ammonium di-hydrogen arsenate Lutz *et al.* and Chapelle give $s_{11}=16.9$, $s_{12}=17.3 \times 10^{-13}$ cm²/dyne, which means a Poisson's ratio of -1.02 . It appears that the measurements on both of these materials need confirming.

The results quoted in I for β -brass are also inaccurate, and have been superseded by the more recent measurements of Lazarus (1949 b) and Artman and Thompson (1952), quoted in table 7A. These results have caused some discussion on the effect of composition of β -brass on the elastic constants (Rinehart 1950, Jones 1952 b). The theory of the elastic constants of β -brass has attracted some attention and contributions to it have been made by Cole and Warren (1952), Isenberg (1951), Jones (1952 a) Samoilovitch (1944) and Zener (1947 b).

The elastic constants of lithium sulphate monohydrate, a monoclinic crystal, have been measured both by Mason (1950 a) and by Bechmann (1952 b). Both workers express their results in terms of a two-fold y -axis, but choose their x - and z -axes differently (see §1.1). Bechmann has transformed Mason's results so as to agree with his (Bechmann's) choice of axes, and these transformed constants, as well as Mason's original ones are given in table 7G. A similar situation exists with regard to di-potassium tartrate (DKT), measurements on which have been made by Mason (1950 a) and by Bechmann and Ayers (1954). In presenting the results of his measurements on sodium thiosulphate, Sundara Rao (1949 d) took the two-fold axis as coinciding with z , and in order to accommodate his values in table 7G, the transformation $x \rightarrow z$, $y \rightarrow x$, $z \rightarrow y$ has been applied to his data.

The accuracy of Sundara Rao's values for orthorhombic sulphur (1950 a) is somewhat limited (Sundara Rao 1955) but, in addition, the values from the original paper require amending. Firstly, the correct values of the stiffnesses c_{13} and c_{23} given in the text of the paper are interchanged in the abstract, and the erroneously interchanged values are quoted in *Physics Abstracts* (54, 1951, No. 3090) and in *Chemical Abstracts* (46, 1952, 312 e). Secondly the original conversions from the stiffnesses c_{pq} to the compliances s_{pq} were wrong; the correct values have been given more recently (Sundara Rao 1954) and are reproduced in table 7F.

The published results for Rochelle salt, ammonium and potassium di-hydrogen phosphates, quartz, sodium chlorate, sodium bromate, sodium chloride, lithium fluoride and pyrites have previously been analysed for variability (Hearmon 1952). A similar analysis for certain other materials is made in table 8. This table shows the average values of the elastic constants, the number (n) of sets of observations, and the coefficient of variation (V) defined as $100 s/\bar{x}$, where s is the standard deviation derived from the range, and \bar{x} is the mean value.

This analysis confirms the earlier conclusions (1952) that the results of different workers are seldom concordant to 1%, and that the discrepancies are often considerably greater than this. These conclusions apply equally to materials of constant composition (copper, potassium bromide, potassium chloride) and variable composition (tourmaline). Attempts have

Table 8. Average Values and Coefficients of Variation of Elastic Constants

s_{pq} in 10^{-13} cm²/dyne; c_{pq} in 10^{11} dynes/cm²

A. Cubic System

Material	<i>n</i>		s_{11}	s_{44}	s_{12}	c_{11}	c_{44}	c_{12}
Copper	4	Mean V	14.5 8	14.6 10	−6.05 10	17.1 1	6.91 10	12.2 2
Potassium bromide	4	Mean V	30.1 6	178 12	−4.3 8	3.51 7	0.569 12	0.575 5
Potassium chloride	6	Mean V	26.6 7	148 9	−3.6 44	3.97 6	0.685 9	0.61 41

B. Hexagonal and Trigonal Systems

Material	<i>n</i>			Suffixes					
				11	33	44	12	13	14
Zinc	7	s_{pq}	Mean V	8.07 3	27.6 3	25.2 3	0.61 125	6.99 10	— —
		c_{pq}	Mean V	16.5 4	6.16 12	3.97 3	3.0 23	5.0 12	— —
Tourma- line	4	s_{pq}	Mean V	3.92 7	6.46 11	15.7 6	−0.83 34	−0.63 75	0.52 44
		c_{pq}	Mean V	27.7 7	16.3 7	6.40 5	6.5 37	3.2 63	−0.69 36

been made to relate the elastic constants to composition in garnets (B. Ramachandra Rao 1945) and in mixed potassium–chromium alums (Sundara Rao 1947), but no general law has yet been found, although some regularities are apparent.

In the case of Rochelle salt, the stiffnesses show a large variability, which is reduced considerably when the elastic constants are expressed

as compliances (Hearmon 1952). It is possible that domain structure may be at least partly responsible for the variability in the elastic constants of Rochelle salt. Another possible cause in this and other materials is the existence of dislocations and other imperfections, a subject that has not so far been thoroughly investigated, although Leibfried (1953) and Dienes (1951) have discussed some aspects of it.

It may be mentioned that variability in physical properties of crystals is not confined to the elastic behaviour. Ballard *et al.* (1951) measured a number of properties of monocrystalline lithium fluoride and found remarkably wide variations. The thermal conductivity, for instance, varied from 190 to 350×10^{-4} c.g.s. units on vacuum grown crystals, and from 210 to 310×10^{-4} c.g.s. units on air grown crystals. The limits of Young's modulus (10^{11} dynes/cm²) were 6.5–7.6 for the vacuum grown crystals and 6.2–7.1 for the air grown crystals.

2.3. Effect of Temperature

A considerable amount of quantitative information is now available concerning the effect of temperature on the elastic constants of single crystals. The materials so far investigated (additional to those mentioned in I) are listed in table 9.

It is not possible to discuss all of these results, but as an example, the measurements on sodium chloride will be taken. The elastic constants of this substance have been measured by a number of workers (Rose I 98, Durand I 30, Hunter and Siegel I 59, and, more recently, by Overton and Swim 1951). The various adiabatic measurements are compared up to 750°K in fig. 2; for purposes of this comparison the data of Hunter and Siegel have been converted from the compliances s_{pq} to the stiffnesses c_{pq} . The comparison shows that the stiffnesses c_{11} and c_{44} decrease with increasing temperature, and also that the discrepancies between the values of these two constants measured by the different workers may amount to about 2%. In the case of c_{12} , the discrepancies are considerably larger; furthermore, the results of Hunter and Siegel indicate a maximum in c_{12} at about 400°K, a result which is not repeated by any of the other workers. Theoretical expressions for the variation of elastic constants with temperature have been given by Born and Huang (1954), but no comparison between these equations and experimental results has yet been made.

Some interest has recently been shown in elastic constants at very low temperatures. Galt (1948) predicted thermodynamically that the change in elastic stiffnesses with temperature would be zero at 0°K, and verified this prediction by measurements on KBr down to 4.5°K. Fine (1954, 1955) has described an apparatus suitable for use from 1.7°K upwards, and has applied it to the measurement of the elastic constants of germanium. He finds that the stiffnesses of this element increase with decreasing temperature down to 20–30°K, below which

they are constant and independent of temperature, in agreement with Galt's prediction. Overton and Gaffney (1955) have measured the elastic constants of copper down to 4°K; Landauer (1954) and Olsen (1955) have worked on tin at the superconducting transition temperature, the

Table 9. Effect of Temperature on Elastic Constants

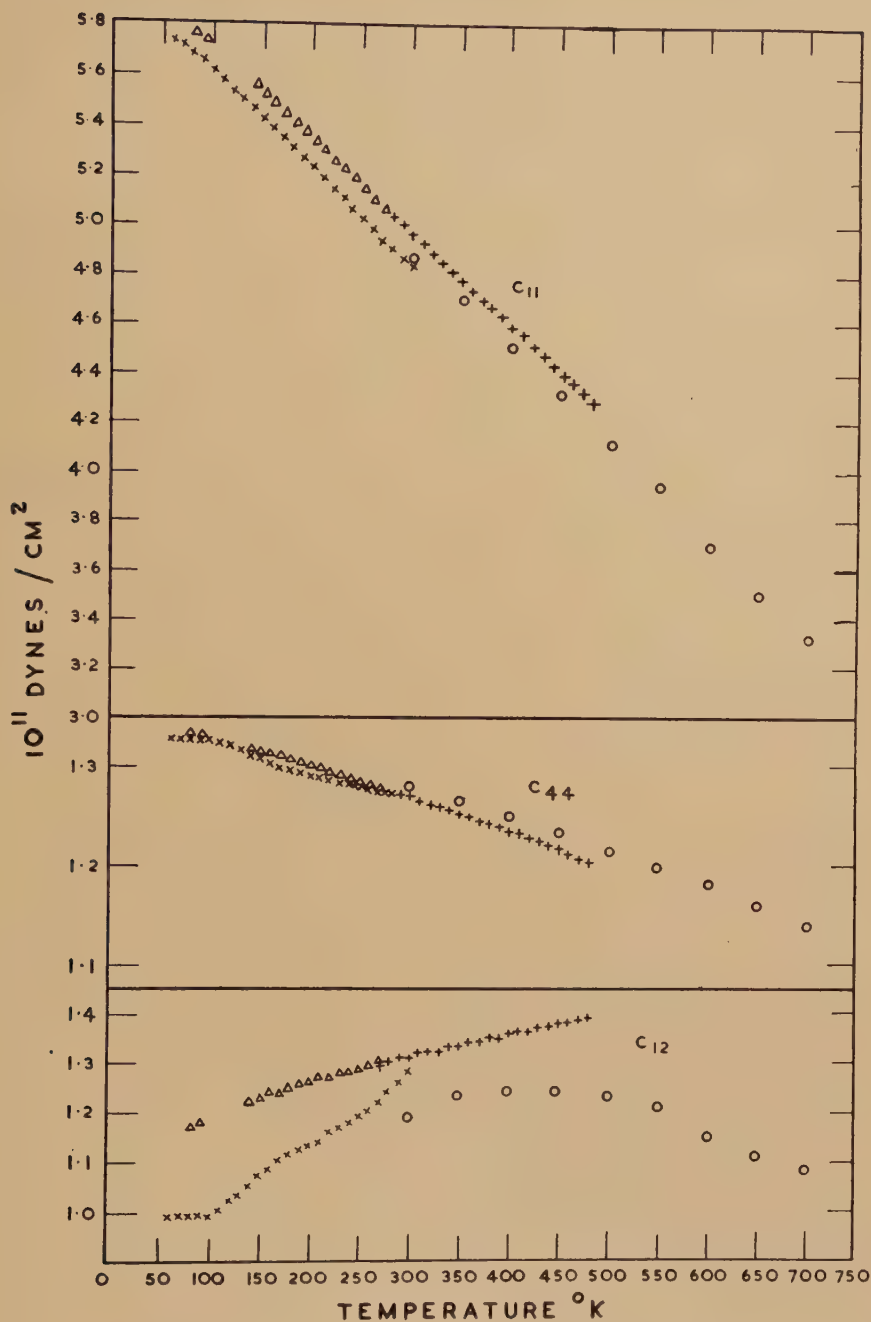
Material	References	Material	References
Aluminium	(17) (19)† (21)	Lithium ammonium tartrate	(12)
A.D.P.	(12) (20)	Lithium potassium tartrate	(12)†
A.D.P.	(13)	Lithium sulphate	(4) (12)
(deuterated)			
Ammonium	(12)†	Lithium trisodium chromate	(12)†
tartrate		Lithium trisodium molybdate	(12)†
Barium formate	(12)†		
β-brass	(1)†	Magnetite	(6)†
Copper	(8) (21)	Potassium bromide	(9)
D.K.T.	(5) (11)	Pyrites	(6)
E.D.T.	(3) (12)	Quartz	(12)
		Rochelle Salt	(10)† (12)
Germanium	(7) (14)		
Gold	(21)	Silicon	(14)
Iodic Acid	(12)	Sodium ammonium tartrate	(12)
Iron	(15)	Sodium bromate	(12)
		Sodium chlorate	(6) (10) (12)
K.D.P.	(2) (12) (20)	Sodium chloride	(16)
K.D.P.			
(deuterated)	(10)†	Strontium formate	(12)
Lead	(21)	Tartaric Acid	(12)
		Zinc	(18)†

† Incomplete data.

References : (1) Artman (1952), (2) Barkla and Finlayson (1953), (3) Bechmann (1950), (4) Bechmann (1952b), (5) Bechmann and Ayers (1954), (6) Bhagavantam (1955), (7) Fine (1953, 1955), (8) Overton and Gaffney (1955), (9) Galt (1948), (10) Jona (1950), (11) Mason (1946), (12) Mason (1950a), (13) Mason and Matthias (1952), (14) McSkimin (1953), (15) Nakamura (1936), (16) Overton and Swim (1951), (17) Sutton (1953), (18) Wert and Tyndall (1949), (19) Yamashita (1953), (20) Zwicker (1946), (21) Goens (1940).

former on single crystals, the latter on polycrystalline material. Application of thermodynamics indicates that the elastic constants should change by about 1 part in 10^5 at the transition temperature. In practice, both workers observe changes of a few parts in 10^6 .

Fig. 2



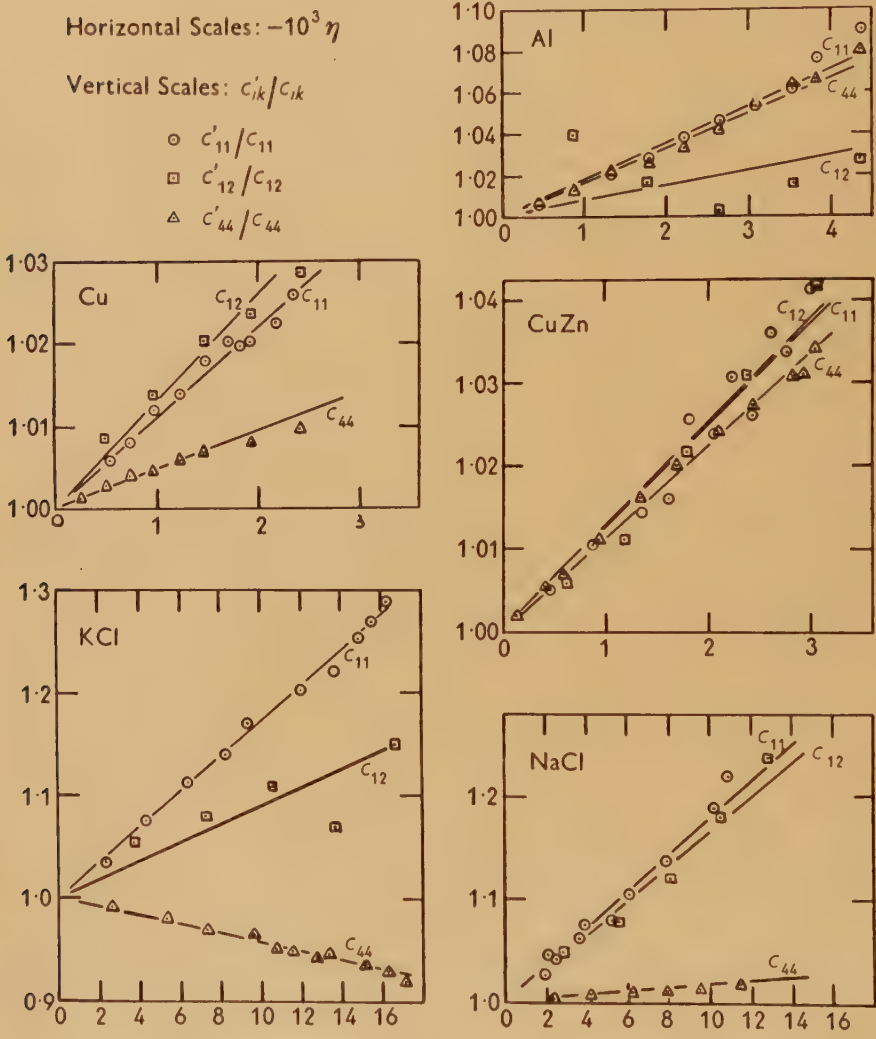
Effect of Temperature on Elastic Stiffnesses of NaCl.

\triangle Rose $+$ Durand \circ Hunter and Siegel \times Overton and Swim

2.4. *Effect of Stress*

Lazarus (1949 a), using a pulse technique, has measured the effect of hydrostatic pressure P up to 10 000 bars on the elastic constants of the cubic materials KCl, NaCl, CuZn, Cu and Al and found the stiffnesses

Fig. 3



Effect of Pressure on Elastic Stiffnesses.

to be linear functions of P in all cases. However, Birch (1947) had previously developed a theory which expresses the effect of pressure in terms of the 'third order' elastic constants (§1.2). According to this

theory, the stiffnesses should depend linearly on the quantity η defined by

$$V/V_0 = (1 + 2\eta)^{3/2},$$

where V_0 is the original volume and V is the volume under pressure P . In fig. 3, the stiffnesses observed by Lazarus are plotted against η , and in each case, a straight line gives a reasonable representation of the observations. Further, from the slopes of the lines, numerical estimates can be made of the following combinations of the third order constants :

$$C_a = 6C_{111} + 4C_{112},$$

$$C_b = C_{123} + 4C_{112},$$

$$C = \frac{1}{2}C_{144} + C_{166}.$$

The resulting values are given in table 10 (Hearmon 1953).

Table 10

' Third Order ' Constants. Unit = 10^{11} dyne/cm²

Material	KCl	NaCl	Cu Zn	Cu	Al
C_a	-81	-100	-208	-249	-225
C_b	- 1.5	- 14	-114	-133	- 32
C_d	- 3.5	- 11	-135	- 84	- 74

All of the constants in table 10 are negative and are numerically about an order of magnitude larger than the stiffnesses.

Hughes and Kelley (1954) have measured the influence of unidirectional stresses on the velocities of wave propagation through isotropic materials and hence have derived values for the three independent third order constants. They show that by making similar measurements on cubic crystals, in conjunction with measurements under hydrostatic pressure, it would be possible in principle to evaluate all the third order constants of cubic materials. However, it should be pointed out that such measurements might be difficult to make, because of the occurrence under unidirectional stress of modes of deformation such as slip or glide, to which the third order constants do not apply.

The change in elastic constants with pressure implies that the frequency of a vibrating crystal should also be sensitive to changes in pressure. Michels and Perez (1951) have investigated the effect of pressure on the frequency of vibration of AT and BT quartz crystals. They find the values of $\Delta f/f\Delta p$, where f is the frequency, to be 8.03×10^{-6} cm²/Kg and -2.03×10^{-6} cm²/Kg respectively for the above two cuts at pressures up to 1000 atmospheres.

Using a similar method, Susse (1955), working with Y, AT and BT crystals found the change of elastic constants with pressure up to 1000 atmospheres to be

$$\begin{aligned}\frac{1}{c_{66}} \frac{dc_{66}}{dp} &= -6.8 \times 10^{-6}, \\ \frac{1}{c_{44}} \frac{dc_{44}}{dp} &= 4.9 \times 10^{-6}, \\ \frac{1}{c_{14}} \frac{dc_{14}}{dp} &= -9.0 \times 10^{-6},\end{aligned}$$

all in cm^2/Kg .

2.5. *Effect of Radiations*

Fron del (1945 b, 1946) showed that the elastic properties of quartz can be altered by exposure to x-rays and to bombardment by electrons, deuterons and α -particles. The aim of these studies was to find a method for the final frequency adjustment of quartz oscillator plates, and Fron del (1945 a) suggested an x-ray method of accomplishing this. During irradiation, there is a decrease in the elastic constants as is shown by a decrease in the resonant frequency of the plates. There is also a development of 'smokiness' in the quartz similar to that sometimes found in the natural material.

Fron del (1946) found that the elastic properties and the colour of irradiated quartz were restored by baking. He also observed an elastic deficiency in natural smoky quartz which was likewise restored by baking, but this finding is in contradiction with the results of B. Krishnamurty (1948), who could detect little change in the density, frequency of vibration or transmission frequency on baking amethyst and smoky quartz specimens.

Bottom (1947) measured the change in certain elastic constants of quartz on irradiation to saturation with x-rays. He found that c_{14} was changed by -0.07% , c_{44} by -0.03% and c_{66} by -0.02% . More recently, Johnson and Pease (1954) have measured the effect of irradiation in an atomic pile on the frequency of vibration of quartz plates, and have found some similarities between the effects of this treatment and those produced by exposure to x-rays. Gordon and Nowick (1955) have irradiated rock-salt with x-rays and found that on well annealed crystals the c_{11} is unaffected, whereas on cold worked crystals, they found changes of up to 5% . Contributions to the theoretical interpretation of the effect of radiation on the elastic constants of metals have been made by Dienes (1952 a, b) and Nabarro (1952), but much remains to be done before the interpretation of effect of radiations in general on all materials is complete.

2.6. *Effect of Electrical Conditions*

The generalized Hook's law, eqns. (1.11) and (1.12) expresses the mutual interaction of stress and strain in the absence of any other

influences. In piezoelectric materials it is possible, by the application of an electric field, to produce a strain in the absence of stress, and, conversely, application of a stress produces not only a strain, but also a separation of electric charge. The values of the compliances s_{pq} and of the stiffnesses c_{pq} will therefore depend on the electrical conditions existing during their measurement. Similar considerations apply to piezomagnetic substances (Voigt I, 115), but these substances have been little investigated and will not be considered here.

From the purely numerical point of view, piezoelectric materials are not very important. There are twelve crystal classes from which piezoelectric phenomena are excluded by symmetry considerations, and these twelve classes between them contain the majority of materials. Even if a material belongs to one of the remaining 20 classes, it will often show insignificant piezoelectric behaviour. Thus, Bond (1943) found that of 830 minerals, only 17 showed appreciable piezoelectric activity. Similarly, Egli (1948) tested 158 water soluble inorganic compounds and found that about 30 showed activity which could be classified as moderate or better; and Mason (1950 a) found that only 41 out of 196 specially selected materials showed useful activity.

However, in spite of their relatively infrequent occurrence, piezoelectric materials have great practical and theoretical significance, for example in the manufacture of electrical transducers, frequency control equipment and filters, and in the development of atomic theories of the solid state (Born and Huang 1954, Wooster 1953).

A number of the most strongly piezoelectric substances such as Rochelle salt, ammonium di-hydrogen phosphate (ADP), potassium di-hydrogen phosphate, (KDP) and barium titanate are 'ferroelectric' (Cady 1946, Mason 1950 a, Baumgartner *et al.* 1950, von Hippel 1952, Jaynes 1953, Devonshire 1954). These materials often have a domain structure, and are markedly non-linear in their behaviour. They exhibit a spontaneous polarization, one consequence of which is an anomalous variation of certain physical properties with temperature. The dielectric constant in the a direction of Rochelle salt, for example, when plotted against temperature, shows two extremely sharp peaks, with the dielectric constant attaining values of several thousands, at temperatures of -18°C and $+24^{\circ}\text{C}$. These temperatures are known as the Curie points; Rochelle salt is, however, exceptional in having two Curie points, since most ferroelectrics have only one. Although work on these substances is of exceptional interest, much of it falls outside the scope of the present review, and only those aspects of it bearing directly on the elastic constants will be discussed. The notation adopted is that of the I.R.E. Standard (1949).

In order to deal theoretically with the interaction between piezoelectric and elastic effects, it is necessary to formulate equations of state involving the strains S_{ij} , the stresses T_{kl} , and an electrical variable, which may be the electric field E_m , the displacement D_m , or the polarization P_m . In

his original formulation, Voigt (I, 115) chose as electrical variable the field E_m , and the generalized Hooke's law (1.11) written in tensor notation and rationalized units then becomes

$$\left. \begin{aligned} S_{ij} &= s_{ijkl}^E T_{kl} + d_{mij} E_m, \\ T_{kl} &= c_{ijkl}^E S_{ij} - e_{mkl} E_m, \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad . \quad (2.61)$$

or where the d_{mij} are the piezoelectric strain coefficients at constant field, the e_{mkl} are the piezoelectric stress coefficients at constant field, and the superscript E to the compliances and stiffnesses also denotes constant field conditions.

However, in 1939, Mason (I, 81) found that when certain elastic and piezoelectric coefficients of Rochelle salt expressed in terms of Voigt's formulation (2.61) were plotted against temperature, extremely wide and sometimes discontinuous changes were observed at the Curie points, but that if surface charge were adopted as the electrical variable, the variation with temperature of the resulting coefficients was in all cases smooth and of a more reasonable magnitude. A little later Müller (I, 85) in 1940 and Cady (1946) worked out the consequences of taking polarization as the electrical variable and found that this also led to a better representation of those coefficients which in the constant field formulation were anomalous.

The original derivations of the equations of state (Cady 1946, 1950, Mason 1950 a) were made by means of thermodynamic potentials, which in their complete form allow for thermal as well as electrical and mechanical effects; the thermal effects are ignored in the present discussion. There has been some controversy over the appropriateness of some of the formulations (Cook 1948, Cady 1948, see also Bechmann 1953 b), and a summary of the various formulations has been made by Haskins and Hickman (1950), who have derived the equations of state directly from the principle of the conservation of energy.

In the I.R.E. Standard (1949), the preferred electrical variable is the displacement D_m , and eqns. (2.61) are then modified to:

$$\left. \begin{aligned} S_{ij} &= s_{ijkl}^D T_{kl} + g_{mij} D_m, \\ T_{kl} &= c_{ijkl}^D S_{ij} - h_{mkl} D_m, \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad . \quad (2.62)$$

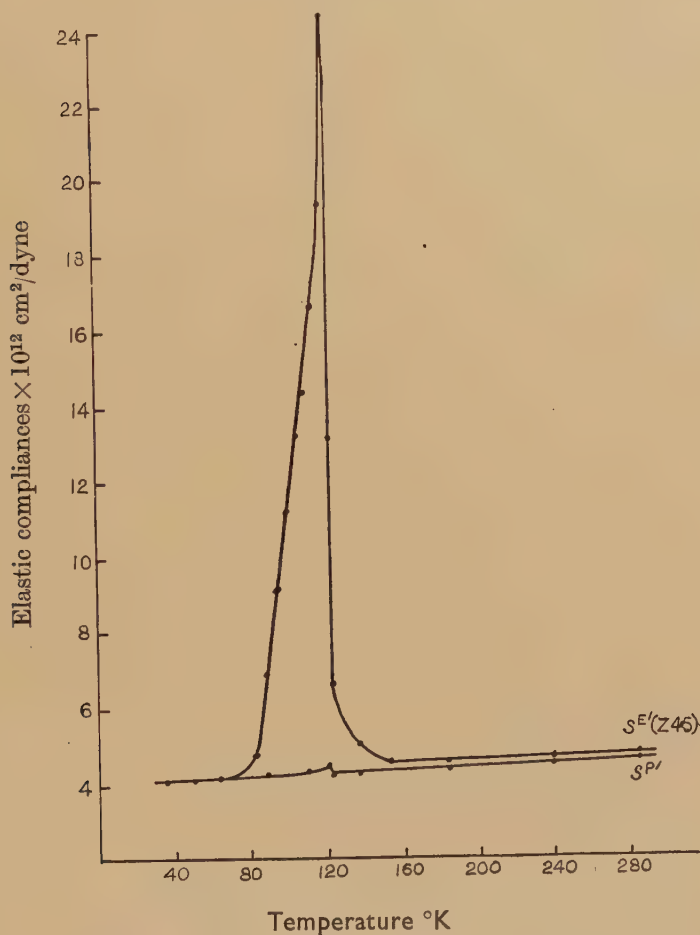
or where g_{mij} is the piezoelectric strain coefficient at constant displacement, h_{mkl} is the piezoelectric stress coefficient at constant displacement, and the superscript D to the compliances and stiffnesses also denotes constant displacement conditions. Bechmann (1953 b) has pointed out that there would be some advantage in amending the notation so that d and e in eqns. (2.61) are replaced by d^E and e^E , and g and h in eqns. (2.62) are replaced by d^D and e^D , since this notation not only emphasises the essential difference between the respective piezoelectric coefficients, but can easily be extended to the case of constant polarization. The equations involving polarization as variable will not be given here; they can be found in Cady's book (1946), and in the papers of Haskins and Hickman (1950) and Bechmann (1953 b).

The complete equations of state lead to a difference between the constant field and constant displacement compliances (or stiffnesses) ; in tensor notation and rationalized units, these differences are

$$\left. \begin{aligned} c_{ijkl}^D - c_{ijkl}^E &= e_{mij} h_{mkl} \\ s_{ijkl}^E - s_{ijkl}^D &= d_{mij} g_{mkl} \end{aligned} \right\} \cdot \cdot \cdot \cdot \cdot \cdot (2.63)$$

Van Dyke and Gordon (1950) have carried out the calculations suggested by eqns. (2.63) for a number of important piezoelectric materials, referred both to principal and to certain rotated axes. They have also carried out the analogous calculations for dielectric and piezoelectric constants ;

Fig. 4



Constant Field and Constant Polarization Compliances (Barkla and Finlayson).

table 11 summarizes these results so far as elastic constants and principal directions are concerned, omitting, however, potassium di-hydrogen arsenate (see table 7D) for which the differences are negligible. Examination of table 11 shows that for the remaining crystals, the differences are usually very small and in many cases are hardly greater

Table 11. Constant Field and Constant Displacement Elastic Constants. s in 10^{-13} cm²/dyne; c in 10^{11} dynes/cm²
(van Dyke and Gordon)

(1) Monoclinic System		Suffixes												
Material	Con- stant	11	22	33	44	55	66	12	13	23	15	25	35	46
Ethylene Diamine Tartrate (EDT)	cE	13.4	3.5	6.04	0.53	0.83	0.57	2.7	8.1	2.2	1.7	0.4	1.2	0.009
	cD	14.0	3.6	6.1	0.55	0.83	0.60	2.7	8.3	2.2	1.7	0.4	1.2	0.01
	sE	38.8	37	98	188	172	174	4.0	-52	-19	-7.0	1.0	-25	-3.0
	sD	37.0	37.0	96.7	182	169	168	3.7	-50	-19	-4.4	1.4	-28	-9.4
Dipotassium Tartrate (DKT) †	cE	6.9	3.5	4.4	0.84	1.3	0.96	1.2	3.2	1.4	0.27	0.18	0.13	0.05
	cD	7.0	3.5	4.4	0.87	1.3	1.1	1.2	3.3	1.4	0.30	0.18	0.11	0.09
	sE	22.4	33.7	38.6	119	81.5	104.1	-0.8	-16.4	-10.5	-6.4	-5.7	9.0	5.7
	sD	22.4	33.5	38.4	116	80.4	95.9	-0.76	-16.4	-10.3	-6.5	-5.3	8.5	9.7
<i>d</i> -Tartaric Acid	cE	9.30	1.93	4.65	0.81	0.82	1.1	2.0	3.7	1.4	-1.2	-0.40	-0.036	0.14
	cD	9.41	1.95	4.71	0.84	0.82	1.1	2.1	3.7	1.4	-1.2	-0.40	-0.045	0.13
	sE	21.6	77	38.5	130	180	96	-6.1	-15	-18	28	28	-29	-16
	sD	21.6	76.9	38.4	120	180	92	-6.1	-15	-18	28	28	-29	-14
Lithium Sulphate Monohydrate†	cE	5.7	7.1	4.9	2.7	2.9	1.4	2.7	1.6	1.6	-0.22	1.6	0.14	0.17
	cD	5.7	8.1	5.0	2.9	2.9	1.4	2.9	1.7	2.0	-0.19	1.7	0.17	0.14
	sE	23.9	21.3	23.1	36.9	41	74	-9.5	-5	-3.6	7.1	-12.0	0.5	-4.6
	sD	23.7	18.9	23.1	35.1	40.7	73.5	-8.9	-4.9	-3.9	6.9	-11.1	0.61	-3.7

† Referred to Mason's axes (1950 a).

Table 11 (continued)
(2) Orthorhombic System

Material	Temp. °C	Con- stant	Suffixes								
			11	22	33	44	55	66	12	13	23
Rochelle salt	+30 and -22	cE	4.3	5.2	6.3	0.58	0.29	0.98	2.9	3.6	3.4
		cD	4.3	5.2	6.3	1.3	0.32	0.99	2.9	3.6	3.4
		sE	51.8	34.9	33.4	172	346	102	-15.3	-21.1	-10.3
		sD	51.8	34.9	33.4	79.6	310	101	-15.3	-21.1	-10.3
	+40 and -28	cE	4.3	5.2	6.3	0.88	0.29	0.98	2.9	3.6	3.4
		cD	4.3	5.2	6.3	1.3	0.32	0.99	2.9	3.6	3.4
		sE	51.8	34.9	33.4	113.4	346	102	-15.3	-21.1	-10.3
		sD	51.8	34.9	33.4	78.7	310	101	-15.3	-21.1	-10.3

(3) Tetragonal System

Material	Temp. °C	Con- stant	Suffixes					
			11	33	44	66	12	13
Ammonium Di-hydrogen Phosphate (ADP)	0	cE	7.1	3.0	0.88	0.62	-2.0	1.3
		cD	7.1	3.0	0.88	0.70	-2.0	1.3
		sE	18	43	113	162	7	-11
		sD	18	43	113	143	7	-11
Potassium Di-hydrogen Phosphate (KDP)	0	cE	8.14	7.85	1.29	0.63	3.49	4.07
		cD	8.14	7.85	1.29	0.65	3.49	4.07
		sE	17.5	20.0	77.5	159	-4	-7
		sD	17.5	20.0	77.9	155	-4	-7

(4) Trigonal System

Material	Constant	Suffixes					
		11	33	44	12	13	14
Quartz	cE	8.75	10.77	5.73	0.765	1.51	-1.72
	cD	8.82	10.77	5.73	0.690	1.51	-1.73
	sE	12.69	9.71	20.05	-1.69	-1.54	4.31
	sD	12.56	9.71	20.04	-1.56	-1.54	4.27
Tourmaline	cE	27.07	16.04	6.68	6.93	0.87	0.77
	cD	27.09	16.19	6.79	6.95	0.93	0.76
	sE	3.98	6.25	15.1	-1.03	-0.16	-0.58
	sD	3.98	6.19	14.86	-1.03	-0.17	-0.56

(5) Cubic System

Material	Temp. °C	Constant	Suffixes		
			11	44	12
Sodium Chlorate	40	cE	5.7	1.2	2.1
		cD	5.7	1.2	2.1
		sE	22	86	-6
		sD	22	86	-6
Sodium Bromate	40	cE	6.2	1.5	2.5
		cD	6.2	1.5	2.5
		sE	21	67	-6
		sD	21	67	-6

than the experimental error of the measurements. The largest differences occur with the s_{44} and c_{44} coefficients of Rochelle salt, and with the s_{66} and c_{66} coefficients of ADP. In general, the differences are largest for ferroelectric materials near their Curie points; this effect is illustrated in fig. 4, due to Barkla and Finlayson (1953). In this figure, the constant field (s^E) and constant polarization (s^P) compliances of a KDP specimen are plotted against temperature. It is evident that the difference reaches a very high value at the Curie point (122°K). Figure 4 also illustrates the advantage of expressing the compliance in terms of constant polarization, for when expressed in this way, the change through the Curie point is relatively smooth, and only a small anomalous variation is observed.

§ 3. APPLICATIONS

3.1. Polycrystalline Aggregates

The relation between the elastic properties of single crystals and of 'quasi-isotropic' bodies made up of a large number of small single crystals disposed at all possible orientations has been considered by many workers. Voigt (I, 115) took the stiffnesses of the aggregate (\bar{c}_{pq}) to be the space averages of the stiffnesses of the single crystals (c_{pq}), a procedure equivalent to assuming that the strain is uniform throughout the assembly, but the stress is not.

Using the abbreviations

$$\left. \begin{aligned} c_{11} + c_{22} + c_{33} &= 3A, \\ c_{23} + c_{31} + c_{12} &= 3B, \\ c_{44} + c_{55} + c_{66} &= 3C, \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad . \quad (3.11)$$

then Voigt's results are

$$\left. \begin{aligned} \bar{c}_{11} &= \frac{1}{3}(3A + 2B + 4C), \\ \bar{c}_{12} &= \frac{1}{3}(A + 4B - 2C), \\ \bar{c}_{44} &= \frac{1}{3}(A - B + 3C). \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad . \quad (3.12)$$

These equations satisfy

$$\bar{c}_{44} = \frac{1}{2}(\bar{c}_{11} - \bar{c}_{12}),$$

and the aggregate is isotropic as far as macroscopic properties are concerned.

The Young's modulus E , rigidity modulus G , and bulk modulus K are given by

$$\left. \begin{aligned} E_V &= \frac{(A - B + 3C)(A + 2B)}{2A + 3B + C}, \\ 5G_V &= A - B + 3C, \\ 3K_V &= A + 2B, \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad . \quad (3.13)$$

where the suffix V denotes the Voigt moduli.

The Poisson's ratio σ is

$$\sigma = \frac{3K - 2G}{2(3K + G)}, \quad . \quad . \quad . \quad . \quad . \quad (3.14)$$

and since only two of the constants of an isotropic material are independent, there is one further relation among the constants; in terms of E , G and K , this relation is

$$\frac{1}{E} = \frac{1}{3G} + \frac{1}{9K}. \quad (3.15)$$

An alternative approach is that of Reuss (1929), who took the compliances of the aggregate \bar{s}_{pq} to be the space averages of the compliances s_{pq} of the single crystals. This is equivalent to assuming uniform stress, non-uniform strain throughout the assembly. The compressibility and rigidity modulus obtained by the Reuss procedure are given by

$$\left. \begin{aligned} 1/K_R &= 3A' + 6B', \\ 5/G_R &= 4A' - 4B' + 3C', \end{aligned} \right\} \quad (3.16)$$

where

$$\left. \begin{aligned} 3A' &= s_{11} + s_{22} + s_{33}, \\ 3B' &= s_{23} + s_{31} + s_{12}, \\ 3C' &= s_{44} + s_{55} + s_{66}. \end{aligned} \right\} \quad (3.17)$$

It should be noted that the Voigt and Reuss expressions (3.12), (3.13) (3.16), (3.17) contain only 9 of the possible 21 independent elastic constants, so that if, for example, the individual crystals are triclinic, then 12 of the single crystal constants do not enter into the expressions for average elastic constants.

For a hexagonal crystal, the non-zero stiffnesses are

$$\begin{aligned} c_{11}, c_{22} (=c_{11}), c_{33}, c_{12}, c_{13}, c_{23} (=c_{13}), \\ c_{44}, c_{55} (=c_{44}), c_{66} (= \frac{1}{2} [c_{11} - c_{22}]). \end{aligned}$$

Thus from (3.11) and (3.12),

$$\left. \begin{aligned} \bar{c}_{11} &= \frac{1}{15} (8c_{11} + 3c_{33} + 4c_{13} + 8c_{44}), \\ \bar{c}_{12} &= \frac{1}{15} (c_{11} + c_{33} + 5c_{12} + 8c_{13} - 4c_{44}), \\ \bar{c}_{44} &= \frac{1}{30} (7c_{11} - 5c_{12} - 4c_{13} + 2c_{33} + 12c_{44}), \end{aligned} \right\} \quad (3.18)$$

which are the Voigt expressions for the stiffnesses of a random assemblage of hexagonal crystals.

In a cubic material $A=c_{11}$, $B=c_{12}$, $C=c_{44}$, and the Voigt eqns. (3.12) and (3.13) become

$$\left. \begin{aligned} \bar{c}_{11} &= \frac{1}{5} (3c_{11} + 2c_{12} + 4c_{44}), \\ \bar{c}_{12} &= \frac{1}{5} (c_{11} + 4c_{12} - 2c_{44}), \\ \bar{c}_{44} &= \frac{1}{5} (c_{11} - c_{12} + 3c_{44}), \\ E_V &= \frac{(c_{11} - c_{12} + 3c_{44})(c_{11} + 2c_{12})}{2c_{11} + 3c_{12} + c_{44}}, \\ 5G_V &= c_{11} - c_{12} + 3c_{44}, \\ 3K_V &= c_{11} + 2c_{12}, \end{aligned} \right\} \quad (3.19)$$

Similarly, the Reuss eqns. (3.17) become for a cubic material

$$A'=s_{11}, B'=s_{12}, C'=s_{44},$$

and therefore from (3.15) and (3.16)

$$\left. \begin{aligned} E_R &= 5/(3s_{11} + 2s_{12} + s_{44}), \\ G_R &= 5/(4s_{11} - 4s_{12} + 3s_{44}), \\ K_R &= 1/[3(s_{11} + 2s_{12})]. \end{aligned} \right\} \quad . \quad . \quad . \quad (3.110)$$

In the cubic system,

$$c_{11} + 2c_{12} = 1/(s_{11} + 2s_{12})$$

and hence

$$K_R = K_V.$$

The above treatments have been reviewed by Stadelmaier (1955) and by Hill (1952) who has compared calculated and observed values of the elastic constants of some cubic materials (table 12).

Table 12. Observed and Calculated Elastic Constants of Polycrystalline Cubic Metals (Hill). Unit = 10^{11} dynes/cm²

Metal	G_R	G	G_V	$K_R = K_V$	K	E_R	E	E_V
Aluminium	2.6	2.65	2.6	7.8	7.4	7.1	7.1	7.1
Copper	4.0	4.36	5.4	13.9	13.3	10.9	11.8	14.4
Gold	2.4	2.78	3.1	16.7	16.6	6.9	7.9	8.7
α -Iron	7.4	8.08	8.9	17.3	15.9	19.3	20.7	22.9

The quantities in table 12 without suffixes are observed values; Hill (1952) and Boas (1947) both point out the difficulty of finding consistent observed values, partly because some preferred orientation may be present, and partly because of experimental error. This difficulty may be illustrated by quoting some of the recently published values for copper and silver (table 13).

Table 13 emphasizes the importance of heat treatment in addition as a contributory factor in the uncertainty. Nevertheless, despite the variability of the results, it is clear from table 12 that in the majority of cases,

$$G_V \geq G \geq G_R; \quad E_V \geq E \geq E_R.$$

Hill has noted that

$$G_V - G_R = \frac{3}{5} \frac{[2c_{44} - (c_{11} - c_{12})]^2}{4c_{44} + 3(c_{11} - c_{12})},$$

and for slightly anisotropic substances, this is a second order quantity. Aluminium single crystals are very nearly isotropic, and this is reflected in the concordance between the Voigt, the Reuss and the observed values.

A similar comparison for certain hexagonal, trigonal and tetragonal metals is given in table 14: for materials belonging to these three systems,

$K_R \neq K_V$ and values of both K_R and K_V are included. The observed values for the polycrystalline materials are taken from the table compiled by Köster (1954).

Table 13. Observed Elastic Constants (10^{11} dynes/cm²) of Copper and Silver

Material	Treatment	E	G	Reference
Ag	?	7.1	2.9	Boas (1947)
Ag (2M)	As received	7.13	3.00	Bradfield and Pursey (1953)
Ag (2M)	$1\frac{1}{2}$ hr. at 550°C	9.60	2.66	
Ag (Isotropic Pure)	Thoroughly annealed	8.28	3.02	
Ag	?	7.89	2.88	Köster (1954)
Cu	?	11.1	4.5	Boas (1947)
Cu	?	11.8	4.36	Hill (1952)
Cu (2M)	As received	12.07	4.75	Bradfield and Pursey (1953)
Cu (2M)	$1\frac{1}{2}$ hr. at 550°C	14.99	4.21	
Cu (2M)	3 hr. at 550°C	14.93	4.20	
Cu (Isotropic Pure)	Thoroughly annealed	12.96	4.83	Köster (1954)
Cu	?	12.3	4.55	

Single crystal magnesium is almost isotropic, and for this material, the Voigt, the Reuss and the observed values are very nearly equal. On other materials the majority of the observed values lie between the Voigt and the Reuss values. Beryllium, cobalt and tin are exceptions, and there is a particularly large discrepancy between K_R and K for beryllium.

Table 14. Observed and Calculated Elastic Constants of Polycrystalline Non-Cubic Metals. Unit= 10^{11} dynes/cm²

Metal	G_R	G	G_V	K_R	K	K_V	E_R	E	E_V
Antimony	2.04	2.00	2.19	3.58	3.63	3.88	5.15	5.49	5.53
Beryllium	11.7	14.7	13.8	24.0	11.5	13.2	30.1	30.9	30.7
Bismuth	0.93	1.20	1.25	3.36	3.24	3.22	2.56	3.19	3.32
Cadmium	1.96	1.92	2.42	4.68	4.76	5.76	5.18	4.99	6.37
Cobalt	6.67	7.62	7.1	18.7	18.3	19.5	17.9	20.4	19.0
Magnesium	1.73	1.74	1.74	3.44	3.33	3.46	4.44	4.43	4.47
Tin	1.50	2.04	1.91	5.28	5.10	5.34	4.10	5.43	5.12
Zinc	3.40	3.72	4.46	5.85	6.05	7.23	8.55	9.22	11.0

Various attempts have been made to refine and improve the theory (Bruggeman 1930, I, 24, Boas 1947, Laurent and Eudier 1950, Hershey 1954); mention may also be made of the work of Lázló (1943, 1944, see also Nabarro 1948) who has attempted to calculate the stress acting

between the individual grains in assemblages of cubic, hexagonal and tetragonal materials.

The treatment by Boas (1947) is based on earlier work by Boas, Schmid and Huber (I, 12, 13, 14, 58). It involves forming the space average of the appropriate modulus (e.g. Young's modulus, shear modulus) over all possible orientations. The result for Young's modulus is

$$E_B = \frac{2K E_N E_X}{E_N + E_X}, \quad \dots \dots \dots (3.111)$$

where the suffix B indicates the Boas value, E_X is the maximum and E_N the minimum Young's modulus for the monocrystalline material and K is the function of $1 - (E_N/E_X)$ plotted at the left of fig. 5 (a) (K is not to be confused with the symbol for bulk modulus used above). A similar formula is obtained for the shear modulus of an assemblage of cubic crystals:

$$g_B = \frac{2K G_N G_X}{G_N + G_X}, \quad \dots \dots \dots (3.112)$$

where K is the function of $(G_X/G_N) - 1$ plotted on the right of fig. 5 (a). Empirically, it is found that eqn. (3.111) gives reasonable agreement with the measured values on the polycrystalline materials, whereas the values calculated from (3.112) are low. This is attributed by Boas to the effects of interaction between the individual crystals. Except for a few special orientations, the twisting of crystals is accompanied by bending (see I, § 5), and, in the polycrystalline aggregate this bending will to some extent be prevented. It is therefore necessary to correct for this effect, and according to Boas, the corrected values are given by

$$\begin{aligned} \frac{1}{G_B} = & \frac{1}{g_B} - \frac{0.3}{E_X} - \frac{1.7}{E_N} + \frac{\frac{1}{2}[(E_X/E_N) - (E_N/E_X)] + 4}{E_X + E_N} \cdot P \\ & + \frac{27}{E_X + E_N} \left(\frac{E_X}{E_N} + \frac{E_N}{E_X} - 2 \right) \cdot Q, \quad \dots \dots (3.113) \end{aligned}$$

where P and Q are plotted in fig. 5 (b) and (c) against

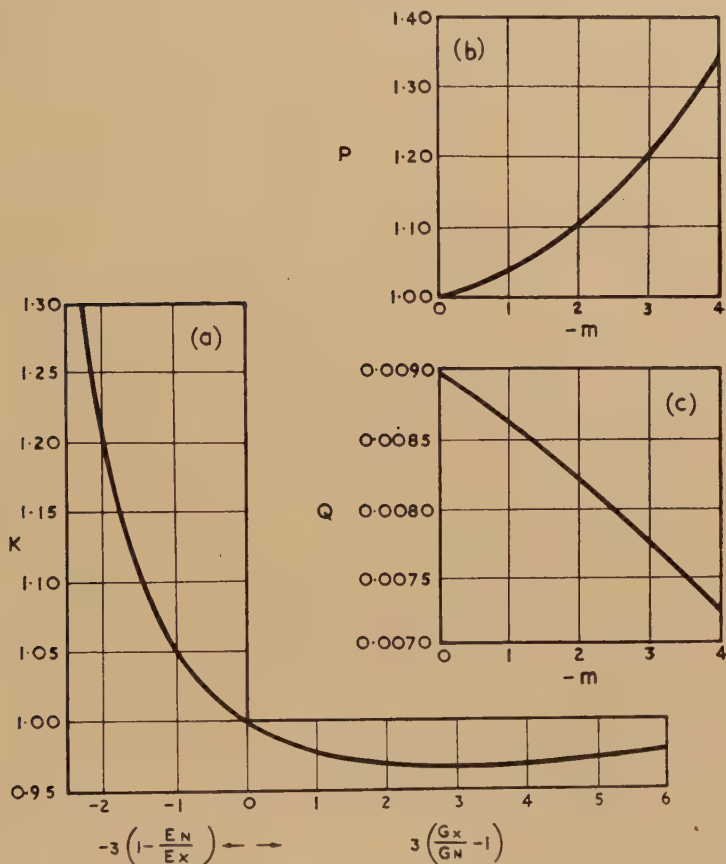
$$m = - \frac{6(E_X - E_N)}{E_X + E_N}.$$

The corrected value G_B is always greater than g_B , the difference increasing with increasing anisotropy; the correction may reach 10% with lead and brass. A comparison of the calculated and measured values of E and G is given in table 15. The first seven substances in this table belong to the cubic system, to which alone eqns. (3.112) and (3.113) apply; cadmium, magnesium and zinc are hexagonal and tin is tetragonal. The values have been converted from those given by Boas.

The elastic constants of polycrystalline aggregates have been applied to the interpretation of the x-ray diagrams of strained materials (Möller 1939, Hershey 1954, Greenough 1955); to the interpretation of the scattering of ultrasonic waves by polycrystals (Lifschitz and Rosentsveig 1946, Roth 1948, Mason and McSkimin 1948, Lifschitz and Parkhomovski

1950, Mason 1950 a); to the correction of elasticity measurements on slightly anisotropic materials (Bradfield and Pursey 1953, Pursey and Cox 1954); to the discussion of the elastic properties of tablets made by compressing alkali halide powders (Bhagavantam and Seshagiri Rao 1952); to the estimation of single crystal constants from measurements made on polycrystalline material (Druyvesteyn 1941, Akulov, Mazin and Feldshtein 1950, Gold 1950 a); and to the interpretation of the elastic after effect in α -iron (Smit and van Bueren 1954).

Fig. 5



Polycrystalline Aggregates (Boas).

3.2. Wave Propagation and the Debye Temperature

The velocities of elastic waves in crystals have been evaluated for certain materials by Grüneisen and Hoyer (1935), Gold (1950 b), Musgrave (1954 b) and others. The velocities are connected with the lattice

dynamics of the crystal (§1.3) and hence with the specific heat (Leighton 1948, Krishnan and Roy 1952, Stepanov 1952, Bauer 1953, de Launay 1953, 1954, Leibfried and Brenig 1953, Born and Huang 1954, Bhatia 1955, Bhatia and Horton 1955). A particularly important

Table 15. Observed (E and G) and Calculated (E_B and G_B) Elastic Constants of Polycrystalline Metals (Boas). Unit= 10^{11} dynes/cm²

Material	E_B	E	G_B	G
Aluminium	7.0	6.9	2.6	2.7
Copper	11.7	11.1	4.5	4.5
Silver	7.3	7.1	2.8	2.9
Gold	7.6	7.8	2.8	2.7
Lead	2.1	1.6	0.8	0.6
α -brass	10.1	11.0	3.9	4.0
α -iron	20.2	20.7	7.9	8.3
Magnesium	4.4	4.3	1.7	1.8
Zinc	9.8	10.0	3.8	3.9
Cadmium	6.0	5.0	2.2	2.0
Tin	4.4	4.5	1.5	1.7

quantity associated with the thermal properties is the Debye characteristic temperature which is given by

$$\theta = \hbar \nu_m / k,$$

where \hbar =Planck's constant,

k =Boltzmann's constant,

ν_m =Debye cut-off frequency.

The cut-off frequency depends on the velocities of wave propagation and is given by

$$\nu_m = v_m \left(\frac{3N}{4\pi V} \right)^{1/3},$$

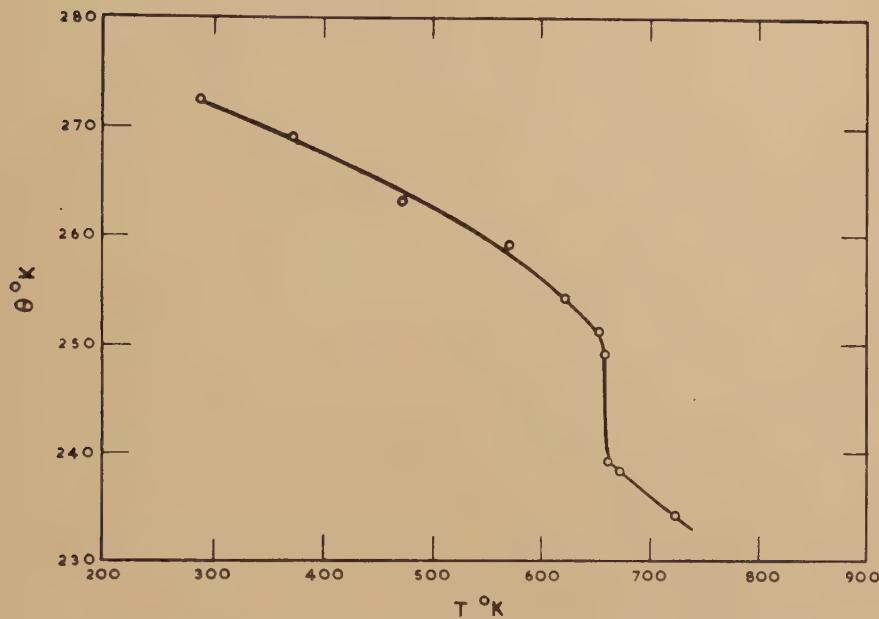
where N is the number of atoms in volume V , and

$$\frac{3}{v_m^3} = \sum_i \frac{1}{v_{mi}^3}, \quad (i=1, 2, 3),$$

v_{mi} being the three velocities of propagation of plane elastic waves averaged over all directions in the crystal. It is thus possible, in principle, to calculate the Debye temperature from the elastic constants, since the velocities are determined by these constants. In practice, however, the calculations are not easy. Blackman (1951) and Post (1953) have proposed semi-empirical methods of calculating θ ; Quimby and Sutton (1953) and Sutton (1955) have discussed the evaluation of a certain integral, with the object of improving the accuracy of the calculations. Characteristic temperatures have been calculated for various materials

by Grüneisen and Hoyer (1935), Blackman (1951), Post (1953), Bradfield (1953) and Bhatia and Tauber (1954). The Debye temperature is normally evaluated from specific heat data, and in table 16, the Debye temperatures given by Post (1953) and Blackman (1951) are compared for some cubic elements.

Fig. 6



Effect of Temperature on Debye Temperature for Cu_3Au (Quimby)

Table 16. Debye Temperatures $^{\circ}\text{K}$

Element		C	Al	Au	Cu	Ag	W	Na	Fe	Li	K	Pb
Post	Elastic Constants	1395	334	162	301	189	286	151	370	—	—	—
	Specific Heat	1860	390	170	315	215	310	150	420	—	—	—
Blackman	Elastic Constants	—	394	158	342	212	—	144	—	354	77	85
	Specific Heat	—	400	160	355	203	—	147	—	(351)	82	91

Post’s method leads to one characteristic temperature for cubic material and to at most three for materials of lower symmetry. Post’s results for some hexagonal and trigonal metal are given in table 17.

Quimby (1954) has calculated θ for Cu_3Au as a function of temperature from the elastic constant data of Siegel (I, 106). In fig. 6, θ is plotted against temperature; the critical temperature for the order-disorder transition is well shown by the sharp drop in θ which occurs at this temperature (661°K).

Table 17. Debye Temperatures $^\circ\text{K}$

Material	Zinc	Cadmium	Mercury
Symmetry	Hexagonal	Hexagonal	Trigonal
$\theta_1 = \theta_2$	268	178	73
θ_3	193	126	89
θ mean { Elastic Constants }	231	152	76
θ { Specific Heat }	250	172	96

3.3. *Miscellaneous*

A general review of anisotropy in metals, particularly anisotropy of thermal, electrical and elastic properties has been made by Boas and Mackenzie (1950).

Mathematical problems associated with the distribution of stress and strain in hexagonal materials have been solved by Elliott (1948, 1949), Shield (1950), Kröner (1953) and Eubanks and Sternberg (1954); and Morse (1954) has discussed the propagation of compressional waves along a cylinder of hexagonal material, the axis of the cylinder coinciding with the hexagonal axis.

Intensive work has been carried out in Russia on the elastic theory of anisotropic bodies, and Fridman (1950) has summarised the resulting contributions. One of the foremost Russian workers, S. G. Lekhnitzkii has published two books, the first (1947) dealing with anisotropic plates, and the second (1950) with the theory of the elasticity of anisotropic bodies. Unfortunately, this work is relatively inaccessible, a factor which has led to some duplication of effort between the Russians and workers in other countries.

The theory of dislocations (see e.g. Kittel 1953) now occupies an important place in solid state physics and provides a means of interpreting some aspects of the mechanical behaviour of solids and of the mechanism of crystal growth. Eshelby (1949) used anisotropic elastic theory to solve the problem of displacements and energy of an edge type dislocation, and further contributions were made by Eshelby, Read and Shockley (1953) Leibfried (1953). Foreman (1955) and Huntington, Dickey and Thomson

(1955). As a sequel to some of this work, Bullough and Bilby (1954) estimated the variation with velocity of the widths of dislocations in the basal plane of magnesium, zinc and cadmium, and Foreman and Lomer (1955) discussed the choice of slip plane in face-centred cubic metals in terms of the dislocation energies.

The theory of anisotropic elasticity and of anisotropic elastic constants has been applied to a number of technological materials, including wood and plywood (Hearmon 1948); keratin (Warburton 1948, Makinson 1954, 1955), laminated plastics, and stiffened plates. The methods suggested by Hearmon and Adams (1952, see § 2.1) were used on laminated plastics by Witt, Hoppman and Buxbaum (1953), and on stiffened plates by Hoppman (1955). Hoppman has further discussed the calculation of deflection under load and of the frequency of vibration of stiffened plates in terms of the elastic constants determined by these methods.

Finally, some mention should be made of 'piezocrescence' a term proposed by Thomas and Wooster (1951) to denote the controlled growth of electrical twinning in quartz under the influence of stress. The phenomenon was apparently discovered by Zinserling and Schubnikov (1933) and has since been also discussed by Frondel (1945 c), Stepanov (1947, 1950), Vormer (1947) and Perez (1952).

Thomas and Wooster's investigations were directed towards the removal of electrical twinning from quartz crystal blanks, thus rendering usable specimens which would otherwise be wasted, and the more practical aspects of the work have been reported by Wooster *et al.* (1947). Thomas and Wooster (1951) showed that it was possible to modify the state of twinning in quartz by the application of stress at elevated temperature, or by subjecting the specimens to a temperature gradient. They propose a theory of piezocrescence according to which the orientation actually developing in the quartz is the one which stores the greater amount of elastic energy. Thus if under a given system of stresses a twinned orientation possesses more elastic energy than an untwinned orientation, then the twinned orientation will tend to develop. Thomas and Wooster found that this theory was able to account largely, though not completely, for the observations on specimens subjected to bending or thermal stress, and to account completely for the observations on specimens in torsion.

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Note added in proof (October 1956). The following references were noted while the above paper was in the press.

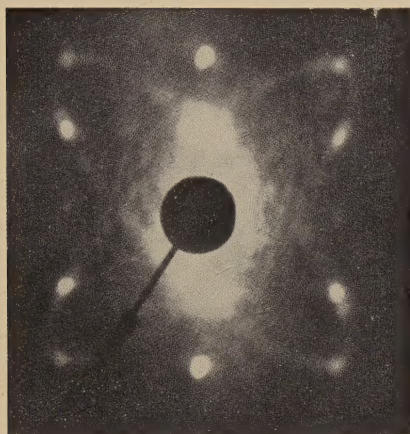
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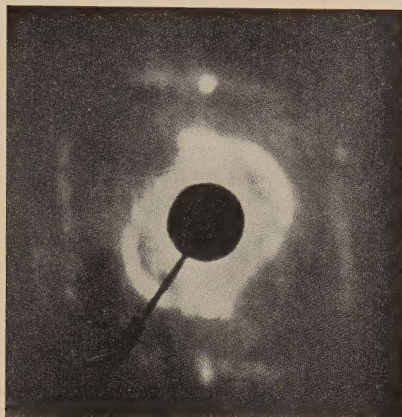
Fig. 1

Light Diffraction by Vibrating Crystals (Zwicker)



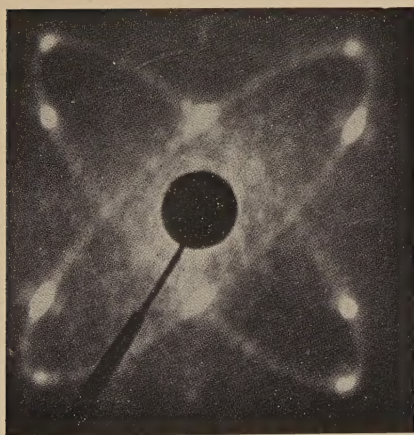
(a)
ADP

Diffraction figure perpendicular
to c axis.



(b)
ADP

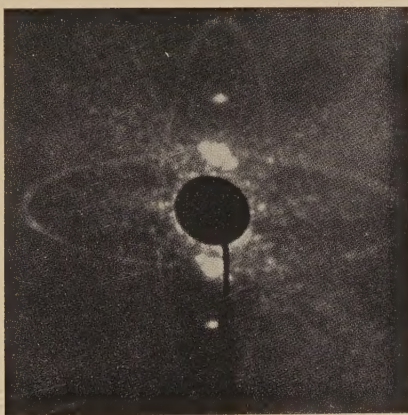
Diffraction figure perpendicular
to a axis.



(c)

KDP

Diffraction figures perpendicular to c axis.



(d)

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